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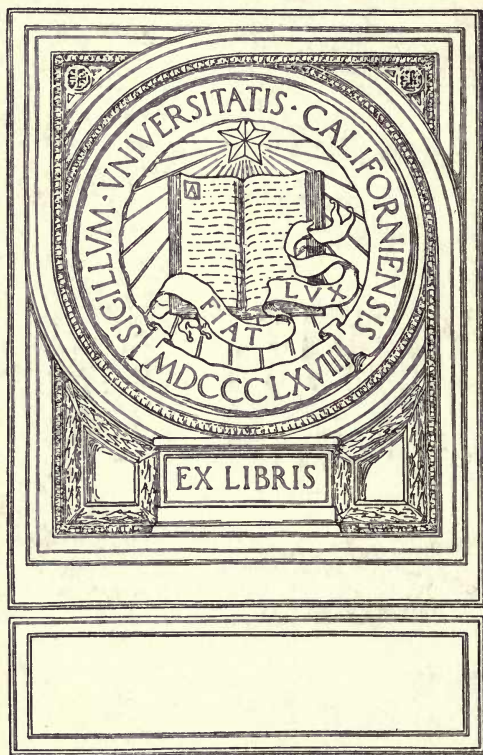
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Harry East Miller



A LABORATORY MANUAL
OF
General Chemistry

For Use in Colleges

BY

WILLIAM C. BRAY,
Professor of Chemistry in the
University of California

AND

WENDELL M. LATIMER
Instructor of Chemistry in the
University of California

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PREFACE

The present laboratory manual has been prepared primarily for the use of students in general inorganic chemistry in the University of California. These students have usually had a year in elementary chemistry in high school, and many of them will take no further work in chemistry. No distinction is made between students on the basis of the various curricula which they are following, as we believe that a course in the fundamentals of general chemistry is equally suitable for all students.

The laboratory and lecture work are correlated as closely as possible. In the present manual page references are given to Professor Joel H. Hildebrand's "Principles of Chemistry," MacMillan, 1918, the reference book written for the course.

The laboratory work is a study of chemical principles, rather than a presentation of descriptive material. It is hoped that the division of the manual into Sections, and the statements in the first paragraphs of the various Assignments, will materially assist the student in recognizing the relation between the experimental details and the principles involved.

When the course extends over two terms, as at the University of California, a satisfactory division is to take Sections I to III in the first term, though in some cases it may be possible also to begin the first Assignment on Qualitative Analysis. It is recommended that the Assignments in the last two Sections be taken in the order noted in the text.

The following editions of the manual have been printed: Laboratory Directions in Chemistry 1A, edited by William C. Bray, 1915; 21 Assignments. A Laboratory Manual of General Chemistry, William C. Bray and Ludwig Rosenstein, 1916; 26 Assignments. The same, revised, by William C. Bray, 1917; 31 Assignments; reprinted 1918, 1919, 1920. The present manual contains 5 Sections with a total of 30 Assignments, and is an almost complete revision of the 1917 manual.

In the development of this manual from 1912 to the present time a great deal has been contributed by the instructors in the course. We wish especially to acknowledge our indebtedness to Professors G. N. Lewis, J. H. Hildebrand, Edward Booth and E. D. Eastman and to Doctors Ludwig Rosenstein and W. L. Argo.

WILLIAM C. BRAY,
WENDELL M. LATIMER.

June, 1921.

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NOTE TO STUDENTS

1. *Decide what is the real purpose of each Assignment.* Before beginning the experimental work and preferably before coming to the laboratory, read the first paragraphs of the Assignment, study carefully the References, and review earlier, related work. In general look for the connection between the lectures and laboratory work and between each Assignment and the preceding ones.

2. *Master each idea* before proceeding to the next one. Form the habit of at once consulting the instructor whenever you are not certain of the correctness of your answer to questions and of your conclusions from the experiments. The frequent short written examinations will be of great assistance to you in deciding whether or not you have really understood the work.

3. *An average student who has understood the earlier work can complete an Assignment in the regular laboratory time allotted to it.* Students who cannot finish in the stated time, announced by the instructor, must consider themselves behind the class, and should plan immediately to do extra work at home and in the laboratory. For their convenience the building is open from 8:00 A. M. to 4:30 P. M. (Saturdays 8:00 to 12:00).

4. *Your success depends upon your own efforts.* If you are in serious difficulty then there is something wrong with your methods. The instructor can assist you in finding out what is wrong, but he cannot do your work for you. No effort on his part can make up for lack of initiative on your part, failure to assume the responsibility of mastering each idea, or inability to improve your method of doing the work.

SPECIAL LABORATORY DIRECTIONS

5. A laboratory note book about 6½ inches wide, opening at the side, and not loose-leaved, is recommended. This book and the laboratory manual will be needed at each meeting of the laboratory section, including the first one.

6. The recording of experiments, observations and conclusions at once in the note book is an essential part of the laboratory work. Entries made from memory or from memoranda on scraps of paper are not records of the experimental work. The value of the original record is improved: by dating each day's notes; by numbering the pages of the note book; by never erasing an entry or tearing out a page; by leaving space for additions and corrections; by adopting a plan of distinguishing between the record of the experiments actually performed, and the other entries such as answers to questions, solutions of problems, etc.; by making all calculations neatly at the bottom or side of the page; and by writing entries in such a way that they will be easily understood when the work is reviewed. The descriptions of the experiments performed should be very brief when detailed directions are given in the manual, but must be complete when, as in the later work, experiments are devised by the student. A passing grade in the laboratory work will not be given unless the experiments have been completed and the results properly recorded in the note book.

7. The laboratory desk must be kept neat and dry. An old towel should be used for cleaning the desk top and another towel should be kept clean for use on apparatus. When cleaning apparatus use tap water and a brush to remove all visible dirt and rinse finally with a little distilled water. Before leaving the laboratory the apparatus should be locked up in the desk.

8. The wash-bottle should only be used to hold distilled water. Before using sterilize the mouth-piece by boiling in water, and never lend or borrow a wash-bottle.

9. The contamination of laboratory reagents can be avoided by keeping each stopper clean and replacing it at once in the proper bottle, and by never pouring anything back into a reagent bottle.

10. Experiments which give rise to disagreeable or dangerous fumes must always be performed out of doors or in a fume-closet.

11. *At the first meeting of each laboratory section the instructor will distribute the desk keys together with lists of apparatus similar to the one given below. Check the apparatus in the locker, exchange damaged articles at the office, sign the list of apparatus (surname first) and return it to the instructor. Begin work on Assignment I.*

LIST OF APPARATUS

1. *Regular equipment of each locker.* Additional articles may be obtained at the office by filling out an "order slip" and signing your name and locker number. Whenever any article is returned to the office sign a "return slip." At the end of the term the locker must contain the same amount of apparatus, no more and no less; the locker must be clean; the apparatus must be clean and dry, and in good condition; glass stoppers must fit, and be protected by the insertion of a piece of paper.

- | | |
|--|--------------------------------------|
| 1 Key. | 1 Casserole. |
| 5 Beakers, 100 cc., 150 cc., 250 cc.,
400 cc., 600 cc. | 1 Crucible, with cover. |
| 5 Reagent Bottles. | 2 Evaporating Dishes. |
| 2 Sample Bottles, 50 cc. | 1 Crucible Tongs. |
| 1 Graduated Cylinder, 50 cc. | 1 Bunsen Burner, with rubber tubing. |
| 4 Flasks, 500 cc., 250 cc., and two
125 cc. | 1 Iron Wire.* |
| 1 Wash-bottle, equipped with glass
tubing and rubber stopper. | 1 Wire Gauze.* |
| 2 Funnels. | 1 Triangle. |
| 2 Blue Glasses. | 1 Test-tube Brush.* |
| 2 Glass Rods, 12 cm. and 18 cm. | 1 Test-tube Holder. |
| 30 cm. Glass tubing.* | 1 Test-tube Rack. |
| 12 Test-tubes. | 1 Package Filter Paper.* |
| 1 Watch Glass. | 1 Rule. |
| | 2 Towels. |
| | Litmus Paper* in a bottle. |

2. The following additional articles may be obtained at the office:

- (a) By signing the regular order slips. Small short-stemmed funnels; glass flasks, 50 cc.; matches *; corks; rubber stoppers.
- (b) By signing "temporary order slips." Special apparatus for Assignments 2 and 4; burettes, with clamps and pinch-cocks; graduated cylinders, 10 cc. and 250 cc.; thermometers; paraffin. These articles should be returned when possible during the same laboratory period.

*Not returnable. At the end of the first term students should retain these articles for use in the second term.

SECTION I

WEIGHT RELATIONS IN CHEMICAL REACTIONS

ASSIGNMENT 1

A CHEMICAL REACTION: THE SYNTHESIS OF A SULPHIDE OF COPPER

References. Hildebrand, Principles of Chemistry, Chapter I, and pages 40-43.

1. In Assignment 1 we shall study quantitatively a chemical reaction in which two *elements*, * a *metal* and a *non-metal* unite to form a *pure compound*. The experiment consists in determining the weight of the compound that is formed from a weighed amount of copper when heated with excess of sulfur. From these experimental data, and the *atomic weights* of the two elements, the relative number of *atoms* of copper and sulfur in the compound will be calculated. *Questions.* If 3.04 grams of a certain metal, when burned in oxygen, yield 5.04 g. of a pure compound of the metal and oxygen, what weight of oxygen will combine with 1.00 g. of this metal? What additional information is necessary before the relative number of atoms of the two elements in the compound can be calculated?

2. *Experiment.* Support a clean porcelain crucible, with a cover, on a triangle and heat with the colorless flame of a bunsen burner to low redness. Let the crucible cool about 10 minutes, and weigh it, with the cover, to 10 milligrams. *Note.* Do not make any weighings until instructions in the use of the balance have been given.

3. While the crucible is cooling obtain from the shelf a clean piece of copper wire, weighing about 1 gram, and weigh it to 10 mg.

4. Place the copper in the weighed crucible and add enough powdered sulfur to cover the copper. Place the cover on the crucible and heat gently (with a small flame) until the sulfur ceases to burn at the edges of the cover, but do not remove the cover while the crucible is hot. Then heat more strongly until the bottom of the crucible just becomes dull red. Again allow to cool about 10 minutes and weigh.

5. Carefully remove the cover and note the appearance of the contents of the crucible, but do not touch the substance. If there is any free sulfur on the cover or the wall of the crucible, replace the cover, heat the crucible and cover, and weigh again. Check the accuracy of the final weight by adding a small quantity of sulfur and repeating the experiment; continue until two consecutive results agree within 10 mg. At the end of the experiment remove the substance formed, break it and describe its properties. Clean the crucible with hot nitric acid in a porcelain dish, wash with distilled water, dry by heating, and check the original weight.

6. *Questions.* What conclusions can you draw from each of the following observations: (a) the properties of the product are different from those of either copper or sulfur; (b) the product appears to be homogeneous and its weight is greater than that of the copper used? What additional evidence is necessary to prove that the product is a pure substance and not a solid solution?

7. *Calculations.* Summarize your experimental results and make the calculations necessary to complete a table similar to the following:

* It is suggested that the student form the habit of writing out the meaning of each italicized word in the text and of giving an example whenever possible.

	First Weighing	Second Weighing	Value Chosen
(a) Weight of crucible	-	-	-
(b) Weight of copper	-	-	-
(c) Weight of crucible and product	-	-	-
(d) Weight of product	-	-	-
(e) Difference between (d) and (b)	-	-	-
(f)	-	-	-

Calculate what the increase in weight (e) would have been if one *gram-atom* of copper had been used in the experiment, and enter in the table as line (f); show this result to your instructor at once. How does this number compare with the atomic weight of sulphur? How many gram atoms of sulfur have combined with one gram atom of copper? What, then, is the simplest *formula* of the substance formed? What is the corresponding *molecular weight*? Write the equation for the reaction, and write out in words what this equation means, in terms of (a) atoms and molecules, (b) gram atoms and *mols*, (c) grams, and (d) pounds.

8. *Problems.* (1) In order to determine the effect of a small error in weighing the copper repeat your calculations, Paragraph 7, using for the weight of copper a value 10 mg. greater than your experimental value. What per cent of the weight of copper is 10 mg.? This would be the percentage error in the weight of copper if a 10 mg. error in weighing had been made. What is the corresponding percentage error in your value for the weight of sulfur that would combine with one gram atom of copper?

(2) Calculate the percentage composition of the copper sulfide formed: (a) from your experimental data, and (b) from the formula and the atomic weights of copper and sulfur. Compare the results.

(3) A sulfide of iron contains 53.8% iron. What is the formula? (In solving this problem consider one gram atom of iron and one gram atom of sulfur as the fundamental units for iron and sulfur. Calculate first the weight of sulfur and then the number of gram atoms of sulfur combined with one or more gram atoms of iron.)

(4) The formulas of hydrogen sulfide and of ferrous sulfide are H_2S and FeS , respectively. What are their molecular weights. What weight of sulfur is contained in one mol of hydrogen sulfide? In one mol of ferrous sulfide? What weight of hydrogen sulfide could be made from one mol of ferrous sulfide?

NOTES ON GLASS MANIPULATION

To bend a piece of ordinary glass tubing, hold it with both hands in a fan-shaped gas flame and rotate it slowly between the thumb and fingers until a $2\frac{1}{2}$ to 3 inch portion is uniformly heated and is soft enough to be bent to the proper angle. Set it aside to cool; glass will remain hot enough to burn the hand for some time after it no longer appears to be hot.

To cut glass tubing, scratch it with a file at the proper place, grasp it firmly on each side of this mark (protecting the hands with a cloth), and bend the tube away from the mark.

Always remove the sharp edges of freshly cut glass at once with a file, or by heating in a gas flame.

To draw down a piece of tubing to a capillary, heat a portion about 1 inch long in an ordinary gas flame to a higher temperature than was necessary in bending the tubing. Hold the tube with both hands and rotate it to ensure uniform heating and prevent the hot portion from sagging. Withdraw from the flame and draw apart slowly to obtain a thick-walled capillary.

ASSIGNMENT 2

THE RELATION BETWEEN THE MASS AND VOLUME OF GASES: THE DETERMINATION OF THE VOLUME OF A MOL OF OXYGEN

References. Hildebrand, Chapter II, and pages 52 and 57

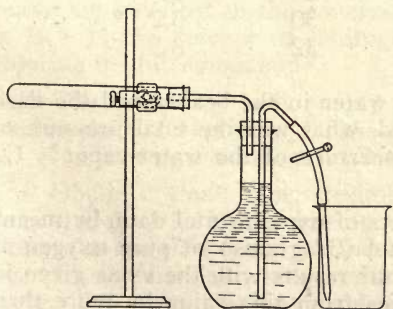
1. It is often necessary to know the volume of a given mass of a substance, or conversely the mass of a given volume. While in the case of a solid or liquid the relation between the mass and the volume must be determined for the particular substance, the problem is simplified when we are dealing with a gas, since a mol of every gas occupies nearly the same volume under similar conditions. In this Assignment we shall determine, under definite conditions of temperature and pressure, the volume of a known weight of oxygen and calculate the volume of one mol at *standard conditions*. *Questions.* What information is needed before you can calculate the weight of 10 cc. of mercury? A given solution of sodium chloride in water contains 25.0 percent sodium chloride and the *density* of the solution is 1.19 g. per cc.; what volume of solution in cc., and in liters, contains 100 grams of sodium chloride?

2. When solid potassium chlorate is strongly heated it decomposes with the evolution of oxygen, and the loss in weight gives the weight of oxygen evolved. The volume of the oxygen is determined by measuring the volume of water displaced by an equal volume of oxygen. When pure potassium chlorate is used it must be heated in a hard glass (difficulty fusible) test-tube. The potassium chlorate decomposes more readily and at a lower temperature when a small quantity of manganese dioxide is present. The hard-glass test-tube may then be replaced by a heavy-walled test-tube of ordinary easily-fusible glass; but care must be taken not to heat the latter tube to a higher temperature than is necessary for the reaction. The manganese dioxide is a *catalyst* in this reaction, and all of it may be recovered after the potassium chlorate has been decomposed into potassium chloride and oxygen.

3. Two students working together obtain from the office a heavy-walled glass tube, a rubber stopper, rubber tube, pinch-cock, clamp and small tube containing about 5 grams potassium chlorate. The yellow order slip for "special" apparatus for Assignment 2 should be signed by both students. The apparatus should be returned as soon as the experiment is finished. Each student must keep a complete record of the experiment in his notebook.

4. *Experiment.* Set up the apparatus according to the accompanying diagram. Since the apparatus must be gas tight, glass tubing and stoppers must be carefully fitted. If your tubes and stoppers do not fit, exchange them at the office. Do not use the glass tubing of your wash bottle. Directions for bending glass tubing are given on page 8.

5. Place in the heavy-walled test-tube about 5 grams potassium chlorate. Add about 50 mg. manganese dioxide, estimating the amount by comparison with the sample in the laboratory; mix it with the potassium chlorate, by jarring the tube; and wipe off any powder that is on the outside of the tube or on the inside near its mouth. Assemble the apparatus as before.



6. Heat the tube gently with a moving gas flame, leaving the pinch-cock open on the rubber tube outlet. Moisture will appear on the walls of the test-tube, which shows that the potassium chlorate and manganese dioxide were not perfectly dry. Gradually warm the tube to within about one inch of the

stopper and at the same time heat the potassium chlorate until gas evolution begins and some water passes over into the beaker. Drive out the moisture with the oxygen by carefully heating the walls of the tube, but do not scorch the rubber stopper. When 50 to 100 cc. water have passed into the beaker, allow the apparatus to cool; close the pinch-cock near the outer end of the rubber tube, which should now be filled with water. Disconnect the chlorate tube, and weigh it with the dry material inside to 10 mg.

7. Immediately replace the tube in its proper position, open the pinch-cock while the end of the delivery tube is under the water, raise the beaker until the surfaces of the water inside and outside the flask are at the same level, close the pinch-cock again, place a dry beaker under the delivery tube, and open the pinch-cock. If the water continues to siphon into the beaker your apparatus is not gas tight and must be rebuilt. Again heat the tube gradually until gas evolution begins, and continue to heat the potassium chlorate carefully and not too strongly until from 250 to 300 cc. water have been forced over into the beaker. Allow the tube to cool, equalize the level of the water in the beaker and the flask, and then close the pinch-cock on the siphon tube. By means of a 250 cc. graduated cylinder measure the amount of water which the oxygen has forced out of the flask. Finally weigh carefully the hard glass tube containing the partially decomposed chlorate. *Question.* Why is it necessary to cool the test-tube and to have the water in the beaker and flask at the same level before closing the pinch-cock?

8. Repeat the *experiment*, Paragraph 7. The three weighings and two volume measurements give two independent sets of experimental data. Compare the results of your two experiments by preparing a table which will show for each experiment: the weight of oxygen, the corresponding volume of water displaced, the data referred to in 10 to 11 below, and the results of the calculations (12).

9. Clean the test-tube by placing water in it and shaking. The manganese dioxide is difficultly soluble in water, while both potassium chlorate and potassium chloride dissolve readily. Suggest a method of recovering the manganese dioxide and obtaining a mixture of dry potassium chloride and potassium chlorate practically free from manganese dioxide.

10. To make the calculations it will be necessary to know the barometric pressure at the time you perform each experiment, and the temperature of the water in the flask. The temperature of the water may be assumed to be that of the room, and the barometric pressure will be posted on the blackboard. Enter these data in your notebook before leaving the laboratory. Below is given a table of the vapor-pressure of water at different temperatures:

Vapor Pressure of Water.

Temp. °C.	Vapor Pressure	Temp. °C.	Vapor Pressure
14	1.2 cm. mercury	24	2.2 cm. mercury
16	1.3 " "	26	2.5 " "
18	1.5 " "	28	2.8 " "
20	1.7 " "	30	3.2 " "
22	2.0 " "	32	3.5 " "

11. *Questions.* Assuming that levels of the water in the beaker and the flask were the same when the pinch-cock was closed, what was the total pressure of the gas in the flask? What was the *partial pressure* of the water-vapor? Of the oxygen?

12. *Calculations.* From each of your two sets of experimental data, by means of the Gas Laws, calculate the volume of 1 mol (32 grams) of pure oxygen at 1 atmosphere pressure and 0° C. Compare your results with the value given in your text book. Your results should not differ from this value by more than

5 percent (check your calculations). Show your tabulated results to your instructor, and repeat the experiment if necessary.

13. *Questions.* What is the formula of the oxygen molecule? What value is usually accepted as a close approximation for the volume of 1 mol of gas under standard conditions? Use this value to calculate (a) the weight of a liter of hydrogen chloride gas, HCl, under standard conditions; (b) the molecular weight of a gas whose density at standard conditions is known to be 0.001977 g. per cc.

14. Write an equation to represent the decomposition of potassium chlorate, KClO_3 , into potassium chloride, KCl, and oxygen; and write out what this equation means in terms of (a) molecules; (b) mols, and (c) grams of the substance involved.

15. *Problems.* (1) One gram of potassium chlorate is completely decomposed into potassium chloride and oxygen. Calculate (a) the weight of oxygen that could be obtained; (b) the volume of the oxygen (in liters and in cc.) at standard conditions, and (c) the volume of the oxygen at 27°C . and 750 mm. mercury pressure.

(2) It is an experimental fact that 2 volumes of carbon monoxide gas react with 1 volume of oxygen to form 2 volumes of carbon dioxide gas. Give the reasoning by which, from this result you can conclude that the molecule of oxygen contains an even number of atoms.

(3) The formulas of carbon monoxide and carbon dioxide are CO and CO_2 , respectively. Write the equation for the reaction considered in the preceding question, and interpret it in terms of (a) mols, (b) liters, and (c) grams.

ASSIGNMENT 3

THE REACTION BETWEEN CERTAIN METALS AND HYDROCHLORIC ACID

References. Hildebrand, pages 84-86, and 47-50.

1. Certain metals, aluminum, zinc, magnesium, etc., react with a solution of an acid, with evolution of hydrogen gas and formation of a salt in solution. In this assignment we shall dissolve a definite weight of a metal in excess of hydrochloric acid, measure under definite conditions of temperature and pressure the volume of the hydrogen liberated, and calculate the weight of the metal that would form one gram-atom of hydrogen. From this result and the atomic weight of the metal we can then determine: the number of atoms of hydrogen formed when one atom of the metal reacts with the acid, the number of molecules of acid (HCl) which react with one atom of metal, and the formula of the chloride of the metal formed. *Questions.* What experimental facts and reasoning have led to the conclusion that the formula of the hydrogen molecule is H_2 ? If the *valence* of hydrogen in HCl is +1 what is the valence of the chlorine in this compound?

2. The instructor will supply to each student a sample of a metal as an "unknown." *Experiment.* Take a portion of the metal weighing between 0.4 and 0.5 g. Clean it, if necessary. Weigh to 5 mg.

3. Obtain a small short-stemmed funnel at the office, and select a beaker of such size that the funnel when placed in it can be completely covered with water. Place the weighed metal in the beaker, place the inverted funnel over it, and pour freshly distilled water into the beaker until the funnel is completely covered. *Note.* Tap water contains a relatively large amount of dissolved air, and should

not be used in this experiment unless it has been heated to boiling to expell the greater part of dissolved air.

4. Pour distilled water into a half liter flask until the water completely fills the flask. Moisten a piece of filter paper slightly larger than the mouth of the flask, cover the mouth of the flask with paper, taking care that no bubble of air remains below the paper. Invert the flask (over an empty vessel) and lower it into the beaker in such a manner that the stem of the funnel enters the neck of the flask. If a bubble of air enters the flask repeat this operation. The apparatus now consists of a beaker containing a funnel inverted over the metal, and a flask filled with water and inverted over the funnel. Place this apparatus in a large beaker or other vessel, to prevent the water from overflowing on the desk during the remainder of the experiment.

5. Insert a thistle tube or long-stemmed funnel into the water so that the lower end touches the bottom of the beaker at the rim of the inverted funnel, and through it pour 25 cc. concentrated hydrochloric acid. If the liquid is not stirred the concentrated acid, which is 1.18 times as dense as water, will remain for some time as a layer at the bottom of the beaker, and the metal will be dissolved rapidly. If all the water in the inverted flask is displaced by the hydrogen you have used too much metal or too small a flask and must begin the experiment over again.

6. When the metal has all dissolved (except a few dark-colored flakes of impurities of negligible weight), place the apparatus in a large basin of tap water and carefully remove the beaker and funnel without allowing any air to enter the inverted flask. Keep the flask in the water for several minutes in order that it may be at the same temperature as the water. Then raise or lower the flask until the level inside and outside the flask is the same. (What is now the pressure of the gas inside the flask?) While the flask is in this position, cover the mouth of the flask with the palm of the hand, remove the flask from the water and invert it. While the gas is escaping, test to prove that it is hydrogen.

7. Measure the volume of the gas which was contained in the flask by filling the flask completely with water and observing the volume needed. Record in your notebook the barometric pressure (written on the blackboard) and the temperature of the water in which the flask was immersed.

8. You now have the weight of metal taken, and the volume, at a definite temperature and pressure, of a corresponding amount of hydrogen saturated with water vapor. What is the partial pressure of the water vapor at the temperature of the experiment? What was the partial pressure of the hydrogen in the flask?

9. *Calculate* from these data:

The volume at standard conditions that the hydrogen would occupy if it were dry.

The weight of the hydrogen. (Use the molecular weight 2.016 and the volume of 1 mol of gas, Assignment 2.)

The weight of metal that would have liberated 1 gram-atom of hydrogen. Report this value to your instructor, who will tell you the name of the metal if your result is correct to within about 5%.

By means of the atomic weight of the metal calculate the number of atoms of hydrogen formed when 1 atom of the metal dissolves in acid.

10. *Questions.* How many molecules of HCl react with 1 atom of the metal? Assuming that the hydrogen of the acid is replaced by the metal, what is the formula of the chloride formed? What is the valence of the metal in this compound? Write the equation for the reaction.

11. *Problems.* (1) From the density of hydrogen at standard conditions,

0.00008987 g. per cc., calculate the actual volume of 1 mol of hydrogen. What percentage error did you make in the calculations in Paragraph 9 by assuming the value 22.40 liters.

(2) If sulfuric acid, H_2SO_4 , had been used in the above experiment instead of hydrochloric acid, the same result would have been obtained and the final solution would have contained a sulfate of the metal. Write the equation for the reaction.

(3) The student will have noted that in the first three Assignments we have assumed a knowledge of atomic weights. The arbitrary choice of the unit $0 = 16.00$ should present no difficulty, but it is often not clear why a particular value is chosen for the atomic weight of an element rather than some fraction or multiple of this value, e.g., in the case of chlorine why 35.46 is chosen instead of say 17.73 or 70.92. To illustrate how this choice is made on the basis of the experimentally obtainable quantities, molecular weight and percentage composition, the following data may be used. (The molecular weights given in the second column of the table are the accurate values, and not approximate values such as would be obtained directly from the weight of 22.40 liters of gas reduced to standard conditions.)

<i>Substance</i>	<i>Molecular Weight</i>	<i>% Chlorine</i>	<i>No. Grams Chlorine in 1 Mol</i>
Chlorine	70.92	100	
Hydrogen chloride	36.47	97.2	
Chlorine oxide (1)	86.92	81.6	
Chlorine oxide (2)	67.46	52.6	
Phosphorus chloride	137.42	77.4	
Carbon chloride	153.84	92.3	

Calculate the values required for the fourth column of the table. What value would you choose for the atomic weight of chlorine? No compound of chlorine has even been made which contains in 1 mol less than 35.46 grams of chlorine. How many atoms of chlorine are contained in a molecule of each of the six substances listed in the table?

ASSIGNMENT 4

THE ANALYSIS OF COPPER OXIDE

Reference. Hildebrand, Chapter III.

1. In this Assignment, as an example of chemical analysis, we shall determine the composition of an oxide of copper. The analysis will be made by heating a weighed portion of the oxide in a current of hydrogen and weighing the metallic copper which remains. The oxygen of the oxide unites with the hydrogen to form steam. As in Assignment 1, we shall determine the formula of the compound by assuming the atomic weights of copper and oxygen. It is to be noted, however, that the results could be used to determine the relative atomic weights of copper and oxygen if the formula of the compound were known. Our experimental data, of course, will not be sufficiently accurate to make worth while the calculation of the atomic weight of copper.

2. *Experiment.* Two students may work together; both should sign the order slip for "special apparatus for Assignment 4," which consists of a thick-walled hard glass test tube with a rubber stopper and glass tubes, a thistle tube, and two-holed rubber stopper, a clamp, and a calcium chloride tube (with 2 rubber stoppers, 2 glass tubes, 2 rubber tubes and 2 short glass rods). The apparatus should be returned as soon as the experiment is finished.

3. Set up a "hydrogen generator" by fitting your half liter flask with a thistle tube extending through the rubber stopper nearly to the bottom of the flask,

and an outlet tube bent at right angles (see note on glass manipulation). Place in the flask about 10 grams of zinc and cover it with about 100 cc. water. To the outlet tube attach a "drying tube" (containing solid calcium chloride, which has the property of absorbing moisture). Make sure that the apparatus is air-tight and wrap the flask in a towel.

4. Set up the remainder of the apparatus according to the directions of the instructor. Dry the thick-walled glass test-tube that is to contain the copper oxide by heating it gently. When it is cool weigh it carefully, together with any portion of the apparatus that may come in contact with the copper oxide. Place in the tube about 1 gram of copper oxide, wipe off any particles that are not in the portion of the tube that is to be heated. Weigh again carefully to obtain the weight of copper oxide used. Attach the apparatus to the hydrogen generator, pour about 40 cc. concentrated hydrochloric acid down the thistle tube, and allow the hydrogen to pass through the apparatus until it has swept out the air. (*Caution.* Do not place a flame near the outlet nor heat the oxide while the apparatus contains a mixture of oxygen and hydrogen. A dangerous explosion might result.) Collect the gas in small test tubes by displacement of water and ignite it. Explain how this test may be used to determine when the hydrogen is no longer mixed with oxygen.

5. When pure hydrogen is passing over the copper oxide, begin to heat the oxide very gently with a small flame and continue to heat cautiously until all the oxide changes color. If moisture collects in the farther end of the tube, drive it out by heating the tube carefully. *Question.* Where does this moisture come from?

6. Allow the tube to cool in the current of hydrogen, and weigh it. If you have time, check this result at once by repeating the heating in the current of hydrogen and then weighing; if not, set the tube aside in order that you may do so if the results of the following calculations are unsatisfactory.

7. Calculate the number of (a) grams; (b) gram atoms of copper that are combined with 1 gram atom of oxygen. What, then, is the formula of this oxide of copper? Repeat the experiment if your results are inconclusive.

8. Write the equation for the reduction of copper oxide by hydrogen, and interpret in terms of (a) atoms and molecules; (b) gram atoms and mols, and (c) grams.

9. Calculate the percents of copper and of oxygen in this oxide of copper (a) from your experimental results; (b) from the formula and the atomic weights of copper and oxygen.

10. *Problems.* (1) The formulas of cuprous oxide and cupric oxide are Cu_2O and CuO , respectively. Write equations for the reactions between the heated oxides and hydrogen to form copper and steam. What weight of copper would be obtained from one gram of each oxide? What is the percentage composition of each oxide?

(2) What weight of water could be obtained from 1 gram of cupric oxide? What volume would this amount of water occupy at 1 atmosphere pressure and (a) 4°C ; (b) 273°C ? What volume of hydrogen at 273°C and 1 atmosphere pressure is required to form this amount of water? Is this the amount that would be used in an experiment similar to the one actually performed?

(3) What are the formulas of cuprous sulfide, cupric sulfide, and hydrogen sulfide? Cuprous and cupric sulfides are also reduced to copper when they are heated in a current of hydrogen; hydrogen sulfide is formed. Write equations for the reactions.

ASSIGNMENT 5

THE REACTION BETWEEN AN ACID AND A BASE IN SOLUTION CONCENTRATION IN TERMS OF MOL% PER LITER

References. Hildebrand, Chapter V, pages 76-80, Chapter VIII, pages 105 and 106.

1. In this Assignment we shall study the reaction between sodium hydroxide and hydrochloric acid in solution and shall determine the amount of salt that is formed from a measured volume of sodium hydroxide solution. In the preceding Assignments the amount of a substance was determined by weighing or by measuring the volume of the pure substance. It is often more convenient to determine the quantity of a substance by measuring the volume of a solution which contains a known amount of the substance in a unit volume of the solution. The amount of the substance in a unit volume of solution is called the *concentration*. *Question.* If the concentration of a salt solution is known to be 10 g. per liter, what volume would you measure out in order to have 0.5 g. of salt?

2. It is necessary first to examine separately the properties of the three solutions, the base, acid and salt. *Experiment.* Prepare dilute solutions of sodium hydroxide, NaOH, and of hydrochloric acid, HCl, by diluting 5 cc. of the laboratory solution of each with 50 cc. of distilled water, and also a dilute solution of NaCl by dissolving between one and two grams of the salt in 50 cc. of distilled water.

To 10 cc. portions of each of the three solutions add a few drops of litmus solution. Repeat using phenolphthalein.

Taste each solution by dipping a glass rod into the liquid and touching it to the tongue. (*Caution.* Do not taste any substance in the laboratory unless directed to do so.)

Test a drop of each solution in a colorless gas flame by means of an iron (or platinum) wire. A yellow flame proves the presence of sodium.

Evaporate to dryness in a casserole 1 cc. of HCl solution, and of NaCl solution. In each case examine if there is a residue. *Question.* What conclusion can you draw in regard to the *volatility* of water and hydrogen chloride as compared to sodium chloride? What result would you predict if a solution containing both NaCl and HCl were evaporated? Pure sodium hydroxide is a stable non-volatile substance which would be left as a solid when a solution containing it is evaporated to dryness. (*Caution.* Do not evaporate alkaline solutions to dryness. Glass and porcelain are slowly attacked by hot concentrated alkaline and a porcelain dish is spoiled if an alkali residue is heated strongly in it.)

Summarize in a table the properties of the three solutions examined above.

3. *Experiment.* Take 40 cc. of your laboratory NaOH solution, place it in a clean half liter flask and dilute with 440 cc. of distilled water. Shake the flask in order that the solution shall be uniform throughout. Cork the flask and label it "NaOH solution for Assignments 5, 6 and 7." *Question.* What approximately is the ratio of the initial volume of the sodium hydroxide solution to the final volume?

4. Dry a porcelain dish and watch-glass large enough to cover it. Weigh the dish and watch-glass to 10 mg. Measure out in your graduated cylinder as accurately as possible 50 cc. of the sodium hydroxide solution prepared above. Pour the solution into the weighed evaporating dish, and sufficient phenolphthalein to give a pink color and then add small portions of your laboratory hydrochloric acid, stirring after each addition, until the solution is colorless. Approximately 5 cc. of the acid will be required to give the colorless solution. If the addition of the last portion of acid is made, a few drops at a time, it will

be observed that the color changes abruptly. An excess of 1 cc. of HCl may now be added.

5. Place the dish containing the solution on your wire gauze and heat until the solution begins to boil. Reduce the size of the flame and allow the solution to boil gently, or to evaporate slowly just below the boiling point, until the bottom of the dish is covered with solid material. Then, to avoid loss from bumping and spattering during the evaporation to dryness, cover the dish loosely with the watch-glass, leaving an open space at one side, and continue the heating, first with a small flame, then more strongly until no further trace of water-vapor is expelled. Allow the dish and residue to cool for 10 minutes while covered with the watch-glass and again weigh to 10 mg. Heat the dish and residue gently for five minutes longer, let cool, and weigh again. If the two weights are not the same within 20 mg. repeat this process until two weights are obtained which check to 20 mg.

6. Dissolve a portion of the residue in a small amount of water and test as in Paragraph 2. State what evidence you have that a reaction has taken place between the acid and base, and that the solid residue obtained is sodium chloride. Write the equation for the *neutralization* reaction between NaOH and HCl and interpret it in terms of (a) molecules, (b) mols, (c) grams of the substances involved.

7. *Calculations.* From the weight of NaCl found in Paragraph 5, calculate (a) the weight of NaOH which must have been present in the 50 cc. of NaOH solution, (b) the number of grams of NaOH in 1 cc. of the solution, (c) the concentration of the NaOH in grams per liter? As we shall see in the next assignment this value may not be very accurate. In addition to errors such as that made in measuring out the volume of the NaOH solution, the laboratory NaOH contains small amounts of impurities, as NaCl.

8. The reaction just considered is typical of the reaction between any acid and any base. In every case H of the acid unites with OH of the base to form water. Write the equations for the reactions between the following bases and acids, and interpret each equation in terms of mols of the substances involved:

Sodium hydroxide and nitric acid

Sodium hydroxide and sulfuric acid (to form two molecules of water)

Barium hydroxide and hydrochloric acid

Barium hydroxide and sulfuric acid.

9. Since the mol is a convenient unit of weight to use in studying chemical reactions, concentration is often expressed in terms of the number of mols of substances in a liter of solution. *Definition.* A solution which contains in one liter one mol of dissolved substance is called a *molal* solution; one which contains in one liter one-tenth mol of dissolved substance is called a *tenth molal* solution, etc. Molal hydrochloric acid is designated thus: M HCl; tenth molal sulfuric acid would be written $0.1 M$ H_2SO_4 , etc. *Questions.* Calculate the number of mols of NaCl obtained in Paragraph 5. How many mols of NaOH were there in 50 cc. of solution? What then is the concentration of your NaOH in mols per liter? If the laboratory solution were exactly $6 M$ (which probably is not the case) what would this concentration be, as a result of the twelve fold dilution in Paragraph 3?

10. *Problems.* (1) How many (a) mols, (b) grams of sulfuric acid are in 50 cc. of $0.2 M$ H_2SO_4 ?

(2) What is the concentration in mols per liter of a solution which contains 5.8 g of NaCl in 125 cc. of solution.

ASSIGNMENT 6

TITRATION OF SOLUTIONS OF ACIDS AND BASES: AN ILLUSTRATION OF VOLUMETIC ANALYSIS

Reference. Hildebrand, Chapter VIII, pages 106-107.

1. In Assignment 5 we learned that an acid and a base in solution will neutralize each other. In Assignment 6 we shall see how this reaction can be used in determining the concentration of one of these solutions when that of the other is known. The operation is called a *titration*. It is evident that a pure solution of a salt may be prepared by mixing the corresponding acid and base in exactly the right proportion; this *end-point* in the titration is determined by means of a suitable indicator. The relative concentration of the two solutions can be calculated when the relative volumes of the two solutions used in the titration are known. *Questions.* How many mols of NaOH are required to neutralize exactly 0.01 mol of (a) HCl, (b) H_2SO_4 ? How many cc. of 0.50 *M* NaOH solution will exactly neutralize 0.01 mol of (a) HCl, (b) H_2SO_4 ?

2. *Experiment.* Prepare 300 cc. approximately 0.5 *M* HCl from your laboratory 6 *M* solution, place it in a flask and shake it. Cork the flask and label it "HCl solution for Assignments 6 and 7." Clean a small flask and label it "known H_2SO_4 solution," rinse the flask with distilled water and set it aside to drain in order to have it ready for use later in this Assignment.

3. *Experiment on the determination of an end-point and the choice of the indicator to be used in the titration.* Dissolve approximately 0.5 g. NaCl in about 50 cc. water, add 2 drops phenolphthalein and stir the solution. Add NaOH solution (approximately 0.5 *M*) drop by drop, stirring after each drop is added, and note how many drops are needed to give a distinct color. Then determine how many drops of your 0.5 *M* HCl solution are required to decolorize the solution. *Note.* Small drops are conveniently added from a glass tube drawn out to a point, the solution being held in the tube by placing the finger over the upper end of the tube. Be sure that the tube is clean; before using, rinse it once with the solution. Repeat the *experiment* with litmus solution instead of phenolphthalein, and determine whether the change in color gives a satisfactory end-point for the titration of HCl and NaOH solutions. Finally determine the nature of the end-point with each indicator when about 1 g. sodium sulfate, $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$ is used instead of NaCl.

4. The volumes of the solutions used in a titration are measured by means of *burettes*; these are uniform glass tubes graduated in cubic centimeters and tenths (or fifths) of cubic centimeters. Two burettes will be placed on your desk before the beginning of the Assignment. At the end of the period rinse them with distilled water and leave them on your desk.

5. *Experiment.* Fill each burette with distilled water. Air may be removed from the small tube below the pinch-cock by tilting the tip upward and allowing the liquid to flow through the pinch-cock. *Question.* Why is it necessary to remove any bubble of air trapped in this small tube? Practice reading a burette: bring your eye to the same level as the liquid and note the reading of the burette corresponding to the bottom of the meniscus; repeat until consecutive readings check to better than 0.05 cc. *Question.* Why is it important to have the eye at the same level as the liquid before making a reading? Never attempt to adjust the volume of the solution in a burette so that the reading will be some exact amount. Allow the water to flow slowly out of the burette. If drops remain on the inner surface of a burette, exchange it at the office for a clean one.

6. Rinse one burette with a little of your approximately 0.5 molal HCl solution, and fill the burette with this solution. Rinse and fill the other burette with the 0.5 molal NaOH solution.

7. Record the readings of the burettes side by side in your note-book; run about 15 cc. of the acid solution into a clean beaker or flask standing on white paper, and record the final burette reading under the initial reading. Add two drops of phenolphthalein, and about 20 cc. distilled water. Then run in the sodium hydroxide solution from the other burette, a little at a time, and towards the end, very carefully, a drop or two at a time, stirring the mixture constantly, until the faintest perceptible permanent pink color is obtained. Wash down the inside of the beaker by means of a jet of water from the wash bottle. If too much of the basic solution is added, decolorize the solution by adding a little of the acid and determine the end-point again. Record the final readings of each burette, and the actual volumes of each solution used in titration. Calculate the volume of sodium hydroxide necessary to neutralize one cubic centimeter of the hydrochloric acid.

8. Repeat this *experiment*, using about 20 cc. of the acid solution, and in each case make the same calculations. Do not fill up the burette each time unless there is not enough solution in it for the titration.

9. *Questions.* If the error in measuring out a volume of solution by means of a burette is 0.10 cc. what is the percentage error if 1 cc. of solution is measured? If 20 cc. of solution are measured? Why is it important not to use less than 10 cc. in any titration?

10. Compare the volume ratios calculated from two titrations. If the result differs from the average by more than 1%, perform additional titrations until you are satisfied that you have determined the volume ratio with an accuracy better than 1%.

11. *Questions.* (a) From an examination of the equation for the neutralization of sodium hydroxide by hydrochloric acid state the ratio of the number of mols of acid and base added to the beaker when exact neutrality was reached.

(b) From your average volume ratio state which solution, acid or base, is the more concentrated, and what is the ratio of the concentrations.

12. Take your clean, dry, labelled flask, Paragraph 2, to the office to obtain a sulfuric acid solution of known concentration.

13. Empty the HCl out of the burette, rinse it with about 5 cc. of the sulfuric acid solution of known concentration, and fill it with the sulfuric acid solution. Determine the volume ratio as before from three (or more) titrations. From the volume ratio and the reaction between sodium hydroxide and sulfuric acid calculate the concentration of the sodium hydroxide solution in mols per liter. Calculate also the concentration of your hydrochloric acid solution.

14. Make a list of the sources of error. (Many of them have been mentioned in the above directions.)

15. Save the remainder of the NaOH and HCl solutions, whose concentration you have determined, in corked flasks for use in Assignment 7.

16. *Problems.* (1) How many cc. of 0.01 M $Ba(OH)_2$ will be required to neutralize 10 cc. of 0.5 M HCl?

(2) What is the concentration in mols per liter of a sulfuric acid solution, 25 cc. of which neutralizes 20 cc. of 0.20 M NaOH?

ASSIGNMENT 7

VOLUMETRIC ANALYSIS, CONTINUED: THE DETERMINATION OF THE EQUIVALENT WEIGHT OF AN UNKNOWN ACID

Reference. Hildebrand, Chapter VIII, pages 108-111.

1. In Assignment 7 there will be introduced another unit of quantity, *the equivalent*. This unit and the corresponding unit of concentration, *equivalents per liter*, are frequently more convenient than the units, mol and mols per liter. The mol and equivalent are identical for HCl, HNO₃, NaOH, NaCl, etc., but a mol of H₂SO₄, Ba(OH)₂ or Na₂SO₄, etc., contains two equivalents. *A solution which contains one equivalent in a liter is called a normal solution and is designated 1 N.* The convenience of this unit of concentration depends upon the fact that when one equivalent of any acid reacts with one equivalent of any base the resulting solution contains one equivalent of the corresponding salt. *Question.* What is the normal concentration of a molal solution of H₂SO₄, NaOH and Na₂SO₄ respectively? How many equivalents of acid can be neutralized by 10 cc. of 0.1 N NaOH? Calculate the normal concentrations of your solutions of NaOH, HCl and H₂SO₄ used in Assignment 6.

2. Weighed portions of an unknown solid acid will be titrated with your NaOH solution. By means of the concentration of the NaOH solution (determined in Assignment 6) the number of grams in one equivalent of the acid will be calculated. The correctness of this result depends of course, on the accuracy of your work in Assignment 6. It is to be noted that if you had started with a solid and of known equivalent weight, you could have used the results obtained in this Assignment to determine the concentration of the sodium hydroxide solution.

3. *Experiment.* Obtain from the office a sample bottle containing approximately 2 grams of a crystalline acid of unknown composition. Clean two $\frac{1}{8}$ liter flasks and label them No. 1 and No. 2. Weigh the sample bottle with its cork and contents. Remove the cork, taking care that none of the solid which may be sticking to it drops off, and shake about one gram into flask No. 1. Replace the cork and weigh again. Shake the remainder of the sample into flask No. 2, and weigh the empty sample bottle and cork. All weighings should be made to 5 mg.

4. Dissolve the contents of each flask in about 50 cc. of distilled water, add two drops of phenolphthalein and titrate to the appearance of the first pink color with the sodium hydroxide solution prepared in Assignment 8. If you should pass the end-point in a titration add from a second burette an acid solution of known concentration until the pink color is discharged, and again titrate to the end-point with the sodium hydroxide.

5. For each sample calculate the number of cubic centimeters of NaOH solution needed to neutralize 1 gram of the acid. If the results differ by more than 2% repeat the experiment.

6. From your two (or more) measurements obtain an average value of the number of cubic centimeters of sodium hydroxide solution per gram of acid. From this average value and the concentration of the NaOH solution calculate the number of mols of NaOH needed to neutralize 1 gram of the acid.

7. *Questions.* How many equivalents are in one gram of the acid? How many grams are in one equivalent of the acid?

Report this value to your instructor at once. If your result is unsatisfactory check your calculations in Assignments 6 and 7 and repeat as much of the work as is necessary.

8. *Problems.* (1) Among the acids suitable for this Assignment are: oxalic H₂C₂O₄ · 2H₂O; citric, H₃C₆H₅O₇ · H₂O; tartaric, H₂C₄H₄O₆ and potassium acid sulfate, KHSO₄. Write the equations for the reaction between NaOH and (a)

oxalic acid to form $\text{Na}_2\text{C}_2\text{O}_4$, and (b) KHSO_4 ; and calculate the equivalent weight of the acid in each of these reactions.

(2) What is the normal concentration of a sulfuric acid solution, 25 cc. of which neutralizes 20 cc. of 0.20 N NaOH?

(3) Chemically pure ("C. P.") sulfuric acid, nitric acid, hydrochloric acid and ammonia, as supplied by the manufacturers, are concentrated aqueous solutions of these substances. The concentration of each solution is guaranteed not to be less than a certain minimum value, and this is tested by measuring the density (or the specific gravity). The following table contains the density and the percentage composition by weight of the concentrated laboratory reagents.

	Density g. per cc.	% by weight	Concentration, Equivalents per liter
H_2SO_4	1.84	95.6% H_2SO_4	
HNO_3	1.42	69.8% HNO_3	
HCl	1.19	37.2% HCl	
NH_4OH	0.90	57.5% NH_4OH	

For each solution calculate the normal concentration and record the results in the fourth column of the table.

Caution! The concentrated acids, especially sulfuric and nitric, produce dangerous burns and should not be used carelessly. When you are directed to use one of these acids carefully pour just enough of it for your experiment into a dry beaker.

SECTION II

IONIC THEORY

RAPID REVERSIBLE REACTIONS AND EQUILIBRIUM

ASSIGNMENT 21

SOLUTIONS OF STRONG ELECTROLYTES. IONIC EQUATIONS

Reference. Hildebrand, Chapter X, pages 124-137.

1. This Assignment, which contains no experimental work, is introduced in order that the student may become familiar with the fundamental ideas underlying the Ionic Theory before proceeding to use these ideas in the following Assignments.

2. The use of the terms acids and bases in designating two distinct groups of substances implies that the members of each group have a set of properties in common. The properties characteristic of all acid solutions, which were observed in Assignment 5, are ascribed to a substance called hydrogen ion, represented by the symbol H^+ ; and those of basic solutions to the substance hydroxide ion, written OH^- . In addition to the properties of the hydrogen ion, each acid in solution has a group of properties different from those of any other acid but common to solutions of all salts of that acid. Thus, hydrochloric acid has a set of properties which is characteristic of solutions of all chlorides and is ascribed to a substance called chloride ion, Cl^- . Likewise, a solution of sodium hydroxide has a group of properties which is characteristic of solutions of all sodium salts and which is attributed to the sodium ion, Na^+ . *Questions.* What is the evidence from freezing point data that there are approximately 2 mols of substance present when one mol of hydrogen chloride is dissolved in water? How does the electrical conductivity of hydrochloric acid solution support the idea that the molecule of hydrogen chloride in solution is broken up into two new substances? In what way does a chloride ion differ from an atom of chlorine, and a hydrogen ion differ from an atom of hydrogen? List briefly differences in properties of the substances hydrogen ion and hydroxide ion.

3. Many substances in dilute solution may be considered as *completely ionized*. These substances are called *strong electrolytes* and include:

Practically all salts

A few acids as HCl , HNO_3 and H_2SO_4 , and

A few bases as $NaOH$, KOH and $Ba(OH)_2$.

The student should memorize this list and should form the habit of thinking of solutions of strong electrolytes in terms of the ions present and not merely in terms of the specific solid, liquid or gas used in making the solution. It is important to realize, however that strong electrolytes are not ionized in the solid or gaseous state; thus, while hydrochloric acid and sodium chloride solutions consist of H^+ and Cl^- and Na^+ and Cl^- , respectively, gaseous HCl and solid $NaCl$ are not ionized, and each has its own specific properties. *Questions.* What are the principal substances present in each of the following solutions and what is the approximate concentration of each substance in mols per liter:

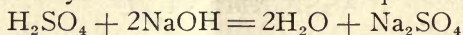
(1) A solution which contains 0.1 mol of H_2SO_4 in 1 liter. (*Answer.* H^+ and SO_4^{--} at concentrations 0.2 *M* and 0.1 *M*, respectively).

(2) A solution which contains 0.2 mol of $NaOH$ in 1 liter.

(3) A solution which contains 0.1 mol of Na_2SO_4 and 0.1 mol of $NaCl$ in 1 liter.

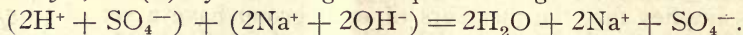
(4) A solution which is made by mixing equal volumes of (1) and (2).

4. *Ionic equations.* Having realized what substances are present in solutions of strong electrolytes we are now in a position to interpret reactions involving such solutions. We shall first consider what is the ionic reaction when a strong acid neutralizes a strong base, and shall take as an example the reaction between sulfuric acid and sodium hydroxide solutions. The equation

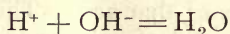


is a statement of the reaction that takes place whenever H_2SO_4 and NaOH solutions are mixed, and we have seen that it may be interpreted in terms of molecules, and of mols, equivalents, grams, or any other weight units. It records no experimental details, such as volumes or concentrations of solutions, or the use of either reagent in excess; and additional notes are necessary when such a record is desired.

This equation can be interpreted according to the ionic theory (a) by adding a note that H_2SO_4 , NaOH and Na_2SO_4 are strong electrolytes and that H_2O is a *weak electrolyte*, or (b) by rewriting the equation to give the same information:



It is evident that the Na^+ and SO_4^- shown to be in the final solution were present in the two initial solutions, and that these substances have undergone no change during the reaction. It is incorrect to say that "sodium ion and sulfate ion have combined." The reaction that has taken place is simply the formation of the weak electrolyte water:



5. The statement that a substance is a weak electrolyte is equivalent to saying that the ions of that substance cannot exist in the presence of each other except at low concentrations and it is obvious that any reaction which involves the formation of a weak electrolyte from its ions may be expected to take place. Accordingly, we shall be able to predict a number of reactions when we have classified the substances involved as strong or weak electrolytes in solution.

6. Another reaction which involves the ions of a strong electrolyte is the precipitation of a *sparingly soluble* salt. Again the statement that a salt, such as silver chloride, AgCl ; is sparingly soluble is equivalent to saying that its ions cannot exist together in solution except at the low concentrations corresponding to the solubility of the salt. Write the ionic equation for the reaction that takes place when dilute solutions containing equivalent amounts of NaCl and AgNO_3 are mixed. What substances are present at high concentrations in each of the initial solutions and in the final solution? Write the ionic equation for the reaction. Consider next the case in which silver nitrate solution in excess is added to a sodium chloride solution, answer the same question and write the ionic equation. It should be obvious that the reaction is the same in both cases, and that, therefore, the two equations should be identical.

7. Does anything happen in the following experiments? A dilute solution of sodium chloride is mixed with a dilute solution of (1) potassium nitrate, (2) nitric acid?

8. *Problems.* (1) Write ionic equations for the following reactions: (a) A precipitate of barium sulfate, BaSO_4 , is formed by mixing solutions of barium chloride and sulfuric acid. (b) A sodium sulfate solution is evaporated to dryness. (c) Hydrogen chloride gas is dissolved in water.

(2) The solubility of lead iodide, PbI_2 , is 0.002 mol per liter at 18° . What is the concentration of the ions present in a saturated solution?

(3) If the freezing point of water is lowered approximately 1.86° per mol of substance in solution in 1000 grams of water, what is the freezing point of a 0.1 molal solution of (a) a non-electrolyte, (b) hydrochloric acid, (c) barium chloride, BaCl_2 ?

ASSIGNMENT 22

STRONG AND WEAK ACIDS. THE USE OF INDICATORS TO MEASURE HYDROGEN ION CONCENTRATION

Reference. Hildebrand, Chapter X, pages 138-142.

1. Indicators can be used to measure the concentration of hydrogen ion, or of hydroxide ion, in a solution. The color change for each indicator occurs in a definite range of concentrations of hydrogen ion (or hydroxide ion), which is characteristic of the indicator. In the present Assignment, by using solutions of known concentration of the *strong acids* listed in Assignment 21, we shall develop a method of determining approximately the concentration of hydrogen ion in any acid solution. This indicator method will then be used to measure the concentration of hydrogen ion in solutions of a typical *weak acid*. Two reactions involving this acid will be studied.

2. *Experiment.* Prepare 60 cc. *N* HCl by adding distilled water to the proper volume of the 6 *N* laboratory reagent and shaking the mixture. From this solution, or from your known HCl solution, Assignment 6, prepare between 50 and 100 cc. of 0.10 *N* HCl, and from this solution prepare 50 to 100 cc. of 0.001 *N* HCl. On account of the error in measuring volumes by means of a graduated cylinder, and the probable variation of the concentration of the laboratory solution from 6 *N*, the concentrations of these solutions are known only approximately.

3. Pour into marked test tubes 10 cc. of each HCl solution (*N*, 0.1 *N*, 0.01 *N*, 0.001 *N*) and pour 10 cc. of water into a fifth test-tube. Add to each solution from a glass tube a single drop of methyl violet solution. Hold the tubes in a vertical position over a piece of filter paper, look down through the surface, record the color of each solution and note the smallest concentration of hydrochloric acid that shows with this indicator a color different from that of water. If the indicator solution is so dilute that one drop does not produce a distinct color add 1 or 2 more drops, but record the number of drops, and use the same number in all the tubes. State how the indicator, methyl violet, may be used to determine the approximate concentration of a hydrochloric acid solution. (The color in the more concentrated solution will fade on standing. It may be restored by adding another drop of the indicator.) *Note.* Set aside the remainder of the 0.01 *N* and 0.001 *N* HCl for use later in this Assignment, Paragraphs 5 and 8.

4. *Experiment.* Repeat the experiment with nitric acid or with sulfuric acid, using the same concentrations as before (*N*, 0.10 *N*, 0.01 *N*, 0.001 *N*). Compare the colors obtained with the different acids. *Questions.* Are the colors characteristic for each acid? If not, what substance determines the color? If hydrochloric acid is completely ionized what conclusion can you draw with respect to the ionization of nitric acid and sulfuric acid? *Note.* Save the 0.001 *N* solution for later use, Paragraph 5.

5. If you have performed the above experiments correctly and understood them you will realize that the indicator methyl violet can be used to determine, approximately, concentrations of hydrogen ion between *N* and 0.001 *N*. However, while the concentration of H^+ in the dilute solution, 0.001 *N*, (which is often written 10^{-3} *N*), is small compared with the normal solution, it is 10,000 times as great as in pure water. We shall now make use of the indicator methyl orange to examine solutions in which the concentration of H^+ is between 10^{-3} *N* and that of pure water, 10^{-7} *N*. *Experiment.* By a 10 fold dilution of your 10^{-3} *N* HCl solution, prepare 50 or 100 cc. 10^{-4} *N* HCl; and from this prepare a 10^{-5} *N* solution. Test 10 cc. portions of these three solutions and of water with 1 drop of methyl orange. Repeat the *experiment* with nitric or sulfuric

acid, starting with your $10^{-3} N$ solution. *Note.* Save one of the $10^{-4} N$ solutions for later use, Paragraph 8.

6. Summarize your results with the two indicators in a table which shows the color obtained at various concentrations of H^+ . Show your table to the instructor.

7. The weak acid which we shall now proceed to study is acetic acid, $HC_2H_3O_2$. It is a white, crystalline, rather volatile solid which melts near room temperature and is very soluble in water. The formula of its sodium salt, sodium acetate, is $NaC_2H_3O_2$. We shall abbreviate these formulas to HAc and $NaAc$, respectively. *Questions.* How many mols of acetic acid are contained in 1 liter of 6 N acid? How many mols of sodium acetate could be prepared from this quantity of acetic acid?

8. *Experiment.* From the laboratory 6 N HAc prepare solutions which are approximately N , 0.5 N , 0.05 N and 0.01 N . Place a 10 cc. portion of each of the acetic acid solutions (N to .01 N) in a labelled test-tube, place 10 cc. distilled water in another test-tube, and test each solution with methyl violet as in Paragraph 3. For comparison, repeat the test with HCl solutions of suitable concentrations. (*Note.* In color comparisons it is not safe to trust the memory, or even written descriptions.) Determine the lowest concentration of acetic acid at which the color with methyl violet is distinctly different from that with water, and estimate approximately the concentration of hydrogen ion in two of the acetic acid solutions, say in the N and 0.1 N solutions. Repeat the *experiment*, but use methyl orange instead of methyl violet, and estimate the concentration of H^+ ion in the 0.1 N solution and in a more dilute solution.

9. The acetic acid in the solution must be present either in the form of ions, H^+ and Ac^- , or in the un-ionized form, HAc . From your estimate of the concentration of H^+ in the 0.1 normal solution, calculate the fraction of the acetic acid which is ionized, and the fraction which is un-ionized. The fraction of the acid which is in the form of ions is called the *degree of ionization*. State also the concentrations of acetate ion, Ac^- , and of the un-ionized acid, HAc , in the 0.1 normal acetic acid solution. Is acetic acid a weak or a strong acid?

10. *Calculations.* The concentration of the ions in acetic acid solutions have been determined by other methods more accurately than is possible by these color experiments. The concentrations of hydrogen ion in these solutions at room temperature are given in the following table:

Concentration acid.	Concentration of H^+ .	Concentration of Ac^- .	Concentration of un-ionized HAc .	Degree of Ionization.
1 N	.004 N			
0.5 N	.003 N			
0.1 N	.0013 N			
0.01 N	.0004 N			

Fill in the remaining columns of the table and show your table to the instructor at once.

11. Memorize the fact that acetic acid and water are weak electrolytes. *Questions.* Refer to Assignment 21, Paragraph 5, and state what you would expect to happen if a solution containing Ac^- at high concentration were mixed with a solution containing H^+ at high concentration. What solutions would you mix to try this experiment, and how could you prove with an indicator that a reaction had taken place?

12. *The reaction between sodium acetate and hydrochloric acid solutions.* *Experiment.* Prepare some approximately half normal hydrochloric acid. Measure out two 15 cc. portions in test-tubes, and add two or three drops of methyl violet to each. Measure 10 cc. 1 N sodium acetate and add the solution,

a few drops at a time, to one of the 0.5 *N* hydrochloric acid solutions. After each addition shake the mixture, record the color and note the volume of the sodium acetate solution added. Write the equation for the reaction that has taken place between H^+ and Ac^- . *Questions.* If solutions containing 0.10 mol HCl and 0.05 mol NaAc were mixed what substances would be present in the resulting solution? What would be the concentration of each if the final volume were (a) 1 liter, (b) 500 cc.?

13. *The neutralization of NaOH solution by acetic acid.* The concentration of H^+ in an acetic acid solution is small in comparison with the *total concentration* of acid in the solution, but the student must not jump to the conclusion that the results of Assignments 5 and 6 on neutralization would have been materially different if acetic acid had been used throughout instead of hydrochloric acid. In the following experiment we shall study qualitatively the reaction between NaOH solution and acetic acid; cf. the quantitative experiment in Assignment 5, Paragraphs 4 and 5. *Experiment.* To 10 cc. 6 *N* NaOH in a porcelain dish add about 8 cc. 6 *N* HAc . (Does the mixture become warm?) Add 1 drop of phenolphthalein and continue to add acetic acid slowly until the solution becomes colorless; test again with the indicator (since the phenolphthalein color fades in a concentrated NaOH solution) and finally add about 2 cc. acid in excess. Evaporate the solution until crystals of salt begin to separate. (*Caution.* Do not evaporate the solution to dryness, since the NaAc may decompose.) Allow the mixture to cool, collect some of the moist salt, $\text{NaAc} \cdot 3 \text{H}_2\text{O}$, and dry it between filter papers. Prove that the salt contains sodium by the flame test, and acetate by warming with 6 *N* sulfuric acid and noting the odor of acetic acid. *Question.* What evidence is furnished by this experiment that the neutralization reaction



takes place when solutions of HAc and NaOH are mixed? The concentration of an acetic acid solution can be determined by titration with a known sodium hydroxide solution when a suitable indicator is used, phenolphthalein in this case (and if time permits the student may perform this titration).

14. We shall now examine the above reaction in the same way as we have already done in Assignment 21, Paragraph 4, in the case of the reaction between a strong acid and a strong base. *Questions.* Which of the four substances are strong and which weak electrolytes? What substance is present at high concentration in an acetic acid solution which is not present at high concentration in a sodium acetate solution? What substance is present in a NaOH solution which is not present at high concentration in sodium acetate solution? What substance is present at high concentration in a sodium acetate solution which is not present at high concentration in either of the initial solutions? Write the equation for the *main reaction*, and show it to your instructor. The study of this reaction will be continued in Assignment 25.

15. *Problems.* (1) 20.0 cc. acetic acid solution were found to neutralize the same volume of NaOH solution as 16.0 cc. 0.50 *N* H_2SO_4 ; phenolphthalein was the indicator in both titrations. What is the concentration of the acetic acid solution (a) in mols per liter, (b) in equivalents per liter, and (c) in grams per liter?

(2) Outline experiments to distinguish between

(a) 1.0 *N* HNO_3 and 0.10 *N* HNO_3

(b) A solution of nitric acid and one of acetic acid which give the same bluish color with methyl violet.

ASSIGNMENT 23

STRONG AND WEAK BASES. THE USE OF INDICATORS TO MEASURE HYDROXIDE ION CONCENTRATION

1. In Assignment 23 we shall develop a method of measuring approximately, by means of indicators, concentrations of hydroxide ion between normal and 10^{-7} normal, the concentration in pure water. This method will be used in studying solutions of a typical *weak base*. Since there is throughout a close relation with the preceding Assignment only brief direction will now be given. The student is expected to make use of the discussion and Questions in Assignment 22 in correlating the results of the two Assignments.

2. *Experiment.* Prepare solutions of sodium hydroxide which are approximately normal, 0.1 normal, 0.01 normal, and 0.001 normal. (State in your note-book how you prepared these solutions.) To 10 cc. of each solution in a test-tube, add 1 drop of a solution of the indicator, trinitrobenzol. Record the color obtained in each case, and observe especially the most dilute solution that gives a color with the indicator. Make a second series of observations using a larger amount of the indicator, say 6 drops, in each case. Note that by using the different amounts of indicator you can determine approximately concentrations of OH^- in one case between N and .01 N , and in the other between 0.1 N and 0.001 N .

3. Repeat the experiment with potassium hydroxide solution, and compare the colors obtained at each concentration. If sodium hydroxide in solution is completely ionized, what conclusion can you draw with respect to potassium hydroxide? What concentrations of hydroxide ion can be measured by means of this indicator, trinitrobenzol?

4. *Experiment.* Prepare solutions of NaOH or KOH which are approximately $10^{-4} N$ and $10^{-5} N$. Test 10 cc. portions of the $10^{-3} N$, $10^{-4} N$ and $10^{-5} N$ solutions, and water with the indicator phenolphthalein. Repeat, using litmus instead of phenolphthalein. *Note.* Since the quantity of alkali in a given volume of these dilute solutions is extremely small it is evident that large errors in concentration may result if the test-tubes and flasks are not thoroughly washed with distilled water before use. Check your results by preparing fresh portions of the 10^{-3} , 10^{-4} and $10^{-5} N$ solutions and repeating the *experiment*.

5. Summarize your results in a table which shows the color obtained with each indicator at various concentrations of hydroxide ion. Compare this table, and the corresponding table in Assignment 22, Paragraph 6, with the table given by Hildebrand on page 181.

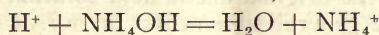
6. In the next experiment we shall determine the concentration of hydroxide ion in solutions of the weak base, ammonium hydroxide, NH_4OH . The concentrated laboratory reagent, cf. Assignment 7, Problem (3), is prepared by dissolving the gas ammonia, NH_3 , in water until the solution is nearly saturated with NH_3 at room temperature. Write the equation for the formation of ammonium hydroxide from ammonia and water. Ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$, is an example of a salt of this base. *Question.* What is the concentration in mols per liter and in equivalents per liter of ammonium ion, NH_4^+ , and of sulfate ion in a 0.1 molal solution of ammonium sulfate?

7. *Experiment.* From the laboratory 6 N NH_4OH solution prepare solutions which are approximately N , 0.1 N , 0.01 N and 0.001 N . By experiments with the indicators trinitrobenzol and phenolphthalein (write out the details of these experiments in your note book) estimate the concentration of OH^- in at least two of these solutions. In each case give also the concentration of NH_4^+ and of un-ionized NH_4OH , and calculate the degree of ionization. *Note.* Accurate

determinations show that at each concentration the degree of ionization of ammonium hydroxide is almost the same as that of acetic acid at the same concentration; see Assignment 22, Paragraph 10.

8. *The reaction between ammonium chloride and sodium hydroxide solutions.* Predict what will happen when a solution of ammonium chloride is added to a solution of sodium hydroxide; cf. Assignment 22, Paragraphs 11 and 12. Plan an experiment to demonstrate this result and try the *experiment*. Write the ionic equation for the reaction.

9. *The neutralization of H_2SO_4 solution by ammonium hydroxide . Experiment.* To 10 cc. 6 N H_2SO_4 in a flask add 6 N NH_4OH from a graduate until the solution, after shaking, has a distinct odor of NH_3 . Evaporate in a porcelain dish until a considerable quantity of salt has separated, cool the mixture, collect some of the salt and dry it between filter papers. Prove that the salt contains (a) sulfate, by dissolving some of it in water and adding barium chloride (to precipitate $BaSO_4$), and (b) the ammonium radical, by warming with sodium hydroxide solution and noting the odor of NH_3 . Give the experimental evidence and reasoning in favor of the conclusion that, when solutions of a strong acid and ammonium hydroxide solutions are mixed, the main reaction is:



The study of this reaction will be continued in Assignment 25.

10. *Problems.* (1) State how you would determine whether an unknown solution is more acidic or more basic than water. (2) Suggest experiments to distinguish between (a) 0.1 N KOH and 0.01 N KOH. (b) A solution of a strong base and one of a weak base which have the same hydroxide ion concentration.

ASSIGNMENT 24

RAPID REVERSIBLE REACTIONS AND EQUILIBRIUM

References. Hildebrand, Chapter XII, pages 155-171; Chapter XI, pages 145 and 148.

1. While certain reactions proceed to completion, as the transformation of metallic copper into cuprous sulfide studied in Assignment 1, many reactions do not. For example, when solutions containing equivalent amounts of a strong acid and sodium acetate are mixed, cf. Assignment 22, Paragraph 12, the resulting solution still contains about 1% of the reacting substances H^+ and Ac^- , i. e., the reaction $H^+ + Ac^- = HAc$, although it takes place very rapidly, stops when about 99% of the possible amount of HAc has been formed. In the final solution, the concentration of the three substances involved in the reaction are the same as in the corresponding acetic acid solution. Similarly, if we had started with pure acetic acid, which is un-ionized in the solid, liquid or gaseous state, and dissolved it in water, the reaction $HAc = H^+ + Ac^-$ would have taken place rapidly, but only until about 1% of the acetic acid had been ionized. *Question.* From your results in Assignment 22, what would be the concentrations of H^+ , Ac^- and HAc in a solution made (a) by dissolving 1 mol of HAc to give a liter of solution, and (b) by dissolving 1 mol of HCl and 1 mol of $NaAc$ to give a liter of solution?

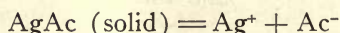
2. The reaction just considered is an example of a rapid, *reversible reaction*, and the three substances involved in this reaction are *in equilibrium* with each other in the final solution. In general whenever it has been shown experimentally that a reaction can be made to take place in both directions, i. e., is reversible, then it may be concluded that under suitable experimental conditions a state of equilibrium can be realized in which all the substances involved in the reaction

are present together. For each set of experimental conditions there is a definite state of equilibrium; and when the experimental conditions are altered, e. g., by changing the concentration of one or more of the substances involved or by changing the temperature the reaction takes place in one direction or the other until equilibrium is again established. The problem is to learn to predict what will happen in any given case when the experimental conditions are altered.

3. *The effect of changing the concentration of one of the substances involved in an equilibrium. Experiment.* Place two 10 cc. portions of *N* acetic acid in two test-tubes, a 10 cc. portion of 0.1 *N* acetic acid in a third test-tube, and a 10 cc. portion of water in a fourth test-tube. To each solution add the same number of drops of methyl violet solution. To one of the normal solutions add a small amount of solid sodium acetate (or of 4 *N* solution); compare the colors of the four solutions. Repeat the experiment with more dilute solutions of acetic acid, using methyl orange instead of methyl violet. *Question.* What conclusion can you draw with regard to the change in the concentration of hydrogen ion in this experiment? What reaction must have taken place? When equilibrium has again been established after the addition of the sodium acetate, is the concentration of each of the substances H^+ , Ac^- and HAc greater or less than its concentration in the original acetic acid solution? State briefly how this experiment illustrates the general statement: *the effect of changing the concentration of one of the substances involved in an equilibrium is to cause that reaction to take place which tends to neutralize the change.* The effect of increasing the concentration of acetate ion could also have been predicted from the quantitative statement of the Mass Law: $(\text{Concentration of } H^+)(\text{Concentration of } Ac^-)/\text{Concentration of } HAc = \text{constant}$, when equilibrium has been established at a definite temperature.

4. Outline an experiment to demonstrate that the reaction $NH_4^+ + OH^- = NH_4OH$ takes place when a solid ammonium salt is added to a solution of ammonium hydroxide; cf. your experiments in Assignment 23. Perform this *experiment*, and explain how it illustrates the italicized statement in the preceding Paragraph.

5. As another example of the effect of change of concentration upon equilibrium we shall study the equilibrium between solid silver acetate and its ions. The reversible reaction is:

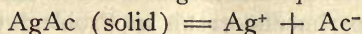


Note. The solubility of silver acetate is 0.06 mol per liter at room temperature; while it is much more soluble than a sparingly soluble salt, as silver chloride, it is much less soluble than such salts as silver nitrate, sodium nitrate or sodium acetate. *Experiment.* Prepare some solid silver acetate by adding to 25 cc. 4 *N* NaAc solution (free from chloride) * about 20 cc. 0.1 *N* $AgNO_3$ solution, and shaking the mixture several times. Collect the solid on a filter paper, and dry it by pressing between dry filter papers. Prepare a saturated solution by shaking the solid with 10 cc. water at intervals for about 10 minutes. (The saturated solution can be prepared somewhat more conveniently by warming the mixture to 40° or 50°, but it must be cooled to room temperature before continuing the experiment). Allow the solid to settle. Pour half of the clear saturated solution into another test-tube and set it aside for later use, Paragraph 7. To the remaining mixture of solid and saturated solution add 6 *N* HNO_3 drop by drop, shaking the mixture after each drop is added. When the silver acetate has dissolved, heat the solution nearly to boiling and note the odor.

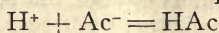
Note. Place all silver residues, including any solution which contain an appreciable amount of silver, in the jar marked "silver waste."

* If chloride is present it may be removed from NaAc solution by adding first some $AgNO_3$ solution, shaking the mixture and filtering off the precipitated $AgCl$. The resulting solution contains some $NaNO_3$ and should be used only in this Assignment.

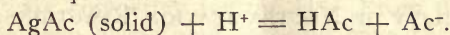
6. The disappearance of solid silver acetate on the addition of a strong acid may be considered to be due to a shifting of the equilibrium



as a result of the establishment of the second equilibrium



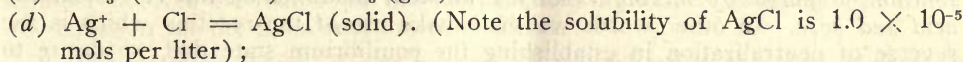
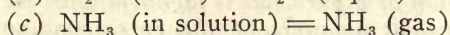
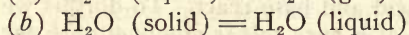
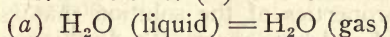
When a drop of nitric acid is added the H^+ uses up Ac^- to form HAc ; and in order to again build up the concentration of Ac^- , and thus restore equilibrium, some solid AgAc goes into solution. When more HNO_3 is added the same processes are repeated, until finally all the silver acetate is dissolved. From this discussion of the *mechanism* of the reaction it is evident that the result of the experiment could have been predicted from the fact that acetic acid is a weak acid. The principal substances that have disappeared are solid AgAc and H^+ , and those that have formed are Ag^+ and HAc ; and we may, therefore, write for the *main reaction* the equation:



The same equation is obtained by adding together the two equations considered in discussing the mechanism of the reaction. It is important, however, to realize that in such a case as this no single equation can represent all that has happened in the reaction. Thus, the concentration of Ac^- , although small throughout the experiment, is much smaller in the final solution than in the initial AgAc solution; this small decrease is due to the reaction $\text{H}^+ + \text{Ac}^- = \text{HAc}$, but is not taken into consideration in the equation which we have written for the main reaction.

7. Predict what will happen when solid sodium acetate is added to a saturated solution of silver acetate. *Experiment.* Test your answer by adding a small amount of 4 *N* NaAc to the clear saturated solution of silver acetate which you have just prepared. *Question.* How does this experiment illustrate the italicized statement in Paragraph 3? Re-word that statement to make it apply specifically to the change of solubility of a salt when the concentration of one of the ions of the salt is changed. What will happen when solid silver nitrate is added to a saturated solution of silver acetate?

8. *Problems.* (1) For each of the following reactions:



outline an experiment to show that the reaction can take place as written and a second experiment to show that the reverse reaction can also take place.

(2) In each case in Problem (1) point out the conditions under which equilibrium can be realized. A satisfactory answer in (a) is the following: whenever water and water vapor are present together in a closed vessel equilibrium is quickly established, and remains unchanged as long as the temperature remains constant; when the closed vessel contains only water and water vapor the pressure at equilibrium is 1 atmosphere when the temperature is 100° ; cf. Assignment 2, Paragraph 10, for the pressure of water vapor at room temperature.

(3) Give an example of a reaction which can be shown to be reversible at high temperature, but which proceeds so slowly at room temperature that equilibrium will not be realized in several months. Note that all the substances involved in this reaction can exist together at room temperature but that such a fact does not constitute a proof that equilibrium has been established.

(4) From your table in Assignment 22, Paragraph 10, state what fraction of

the acetic acid is ionized in the 0.1 *N* and 0.01 *N* solutions. What reaction takes place when 1 liter of 0.1 *N* solution is diluted to 10 liters of 0.01 *N* solution?

(5) State how the experimental result in Problem (4) could have been predicted from *kinetic* considerations, on the assumption that the two opposing reactions, $\text{HAc} = \text{H}^+ + \text{Ac}^-$ and $\text{H}^+ + \text{Ac}^- = \text{HAc}$, are actually taking place at equilibrium.

(6) When one of the substances involved in an equilibrium is a solid, what is the effect of adding more of this solid to an equilibrium mixture? Does the solubility of a salt at room temperature depend on the amount of the salt in contact with the saturated solution? Give another example of a reversible reaction involving a solid substance.

ASSIGNMENT 25

THE REVERSIBILITY OF NEUTRALIZATION REACTIONS. HYDROLYSIS

References. Hildebrand, Chapter XIII, pages 185-192; as a review, read pages 173 and 180-183.

1. In earlier Assignments we have studied various examples of neutralization reactions and have shown that the main reactions that take place are represented by the following equations:

(a) $\text{H}^+ + \text{OH}^- = \text{H}_2\text{O}$ when a strong acid reacts with a strong base.

(b) $\text{HA} + \text{OH}^- = \text{H}_2\text{O} + \text{A}^-$ when a weak acid reacts with a strong base.

(c) $\text{H}^+ + \text{BOH} = \text{H}_2\text{O} + \text{B}^+$ when a strong acid reacts with a weak base.

In the present Assignment we shall find that these reactions are reversible and we shall study the equilibrium that is established in each case. When the Assignment is finished the student should be able, from a knowledge of the relative strengths of various acids, and of various bases, to predict the approximate concentrations of the various substances at equilibrium in any given neutralization reaction.

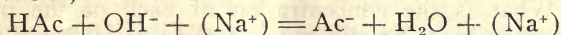
2. We wish to examine experimentally the properties of the solution that is obtained when equivalent amounts of a given acid and base react. To do this we shall take advantage of the fact *that a solution of a pure salt is identical with the solution prepared by mixing exactly equivalent amounts of the corresponding acid and base.* In other words we shall make use of the reaction which is the reverse of neutralization in establishing the equilibrium state that we desire to study. The experimental work will consist in determining by means of indicators the approximate concentration of H^+ or OH^- in solutions of various salts. *Note.* In the following experiments it is important that all test-tubes should be clean; rinse each several times with distilled water before using it.

3. *Experiment.* Test 10 cc. portions of *N* NaCl solution and distilled water by adding to each the same number of drops of litmus solution. Repeat using phenolphthalein and methyl orange. *Question.* What conclusions can you draw with regard to the relative concentration of H^+ or OH^- in sodium chloride solution and in water? Write the ionic equation for the neutralization of NaOH by HCl solutions, and state whether the Na^+ and Cl^- are involved in the reaction. In pure water concentrations of H^+ and OH^- are the same and equal to 10^{-7} mols per liter, what are the concentrations of Na^+ , Cl^- , H^+ and OH^- in the solution made (a) by dissolving 1 mol NaCl in water to give a liter of solution, and (b) by dissolving exactly 1 mol of HCl and 1 mol of NaOH to give a liter of solution?

4. *Experiment.* Test 10 cc. portions of 4 *N* NaAc and distilled water first

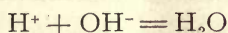
with litmus solution and then with phenolphthalein. Estimate approximately the concentration of OH^- in the 4 *N* NaAc solution. *Questions.* Is the concentration of OH^- in 4 *N* NaAc solution greater or less than in pure water? From the fact that the solution must be identical with that obtained by mixing exactly equivalent amounts of acetic acid and sodium hydroxide, what conclusions can you draw with regard to the completeness of the neutralization reaction between HAc and OH^- ? To account for the formation of OH^- when NaAc is dissolved in water, what reaction must take place? What are the approximate concentrations of Na^+ , Ac^- , HAc and OH^- in the 4 *N* NaAc solution?

5. It will be observed that the main reaction which accounts for the neutralization of HAc by NaOH,

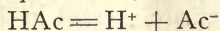


or the reverse of this reaction considered in the preceding paragraph, involves the disappearance of one weak electrolyte and the formation of another. Both the OH^- and the Ac^- are competing for the H^+ . From the fact that water is a far weaker electrolyte than acetic acid, it could have been predicted that when equilibrium is reached the OH^- will have taken nearly all the H^+ away from the Ac^- ; i. e., the concentration of the HAc and OH^- will be very small and that of the Ac^- large. *Question.* From your table of the concentrations of H^+ in acetic acid solutions, Assignment 22, what is the ratio of the concentration of H^+ in *N* acetic acid to that in pure water?

6. As indicated in the preceding paragraph, the *mechanism* of this reaction may be considered to be parallel to that of the dissolving of silver acetate in a solution of a strong acid, Assignment 24. When an acetic acid solution is neutralized by NaOH solution, the OH^- unites with H^+ which is present at small concentration in the acetic acid solution:



and, in order to again restore equilibrium, the HAc dissociates,



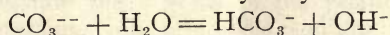
These two reactions continue to take place simultaneously until equilibrium is established. The sum of the two gives the equation which we wrote for the main reaction.

7. Discuss in a similar way the mechanism of the reaction between Ac^- and H_2O which takes place when sodium acetate is dissolved in water. This, of course, involves the reverse of the two reactions written in Paragraph 6. Write the equation for the main reaction in this case.

8. The reaction which is the reverse of neutralization is called *hydrolysis*. In the reaction which we have just considered a small amount of the acetate ion is said to be *hydrolyzed*. *Question.* Why would you expect the Ac^- to be hydrolyzed slightly while the Cl^- is not hydrolyzed at all?

9. The dissociation of HCO_3^- , bicarbonate ion, into H^+ and carbonate ion, CO_3^{--} , is far less than the dissociation of acetic acid. *Questions.* What reaction would you expect to take place between CO_3^{--} and H_2O when Na_2CO_3 is dissolved in water? Which would you expect to be the more basic, a solution of Na_2CO_3 or a solution of NaAc of the same molal concentration? Test your answer by the following experiment

10. *Experiment.* Estimate the approximate concentration of OH^- in a 0.5 *M* Na_2CO_3 solution by testing 10 cc. portions with litmus, phenolphthalein and trinitrobenzol. The main reaction for the hydrolysis of CO_3^{--} is



and the concentration of OH^- in a 0.5 *M* Na_2CO_3 solution is about 0.01 *M*. *Questions.* What would be the concentration of OH^- if the CO_3^{--} were completely

hydrolyzed? What fraction of the CO_3^{--} has been hydrolyzed? What would be the approximate concentrations in mols per liter of Na^+ , CO_3^{--} , HCO_3^- and OH^- in a solution prepared by dissolving 0.05 mol NaHCO_3 and 0.5 mol NaOH to give 1 liter of solution?

11. *Experiment.* Test a 10 cc. portion of 4 *N* NH_4Cl with litmus solution. Compare the color with that obtained by adding the same amount of litmus solution to (a) 10 cc. water and (b) 10 cc. water containing 1 drop of 6 *N* HCl . *Questions.* How do you account for the fact that a solution of NH_4Cl is slightly acid while that of NaAc is slightly basic. Write the main reaction for the hydrolysis of the NH_4^+ , and the two reactions which may be used to explain the mechanism of the reaction. The concentration of H^+ in 4 *N* NH_4Cl is about 4×10^{-5} *N*. What is the concentration of each of the principal substances present in a solution made by dissolving 4 mols of HCl and 4 mols of NH_4OH to form a liter of solution?

12. *Problems.* (1) What is the concentration of H^+ in *N* NaOH ? *Note.* Consult Hildebrand, page 180.

(2) From the results of the experiments in this Assignment and the table of indicators (Hildebrand, page 181) select one or more indicators which might be used to determine the end-point (i e., to determine when equivalent amounts of acid and base are present) in each of the following titrations:

- (a) NaOH solution with HCl or HNO_3 solution.
- (b) HAc solution with NaOH solution.
- (c) NaHCO_3 solution with NaOH solution.
- (d) NH_4OH solution with HCl solution.

Note. Compare Assignment 6, Paragraph 3.

(3) An ammonium acetate solution gives the same colors with indicators as does water: What hydrolysis reactions must occur when solid NH_4Ac is dissolved in water? State what substances are present in the solution.

(4) Point out parallelisms between the strengths of acids and bases and the hydrolysis of the corresponding ions.

SECTION III

REACTIONS OF IONS

ASSIGNMENT 31

THE PROPERTIES OF SODIUM, POTASSIUM AND AMMONIUM IONS. TESTS FOR CHLORIDE, SULFATE AND NITRATE IONS

Reference, for Assignments 31 and all later Assignments: A Standard Text on Inorganic Chemistry.

1. In this Assignment we shall study the properties of the ions of the common acids and bases.

2. Aside from the physical properties, such as color and taste, the properties of an ion depend on its behavior toward other substances. The study of the *chemistry of an ion* thus consists in determining whether or not various substances react with the ion, and in studying the reactions that do take place. For each reaction it is necessary to know:

- (1) the products of the reaction,
- (2) whether the reaction takes place rapidly or slowly,
- (3) whether the reverse reaction can be made to take place, and
- (4) the nature of the equilibrium if the reaction is rapid and reversible.

In this course the task is greatly simplified on account of the following considerations: Nearly all the reactions studied take place very rapidly; this is characteristic of ionic reactions, such as ionization, precipitation, neutralization, etc. Also the number of different types of reactions is not large; and, when for one type a single example is understood, additional examples should present no real difficulty. Finally an equilibrium state is reached in many cases, and a knowledge of the principles of equilibrium enables the student to predict what will happen when there is a given change in the experimental conditions. While the number of facts to be remembered is thus greatly reduced, it is necessary, however, to *memorize* such facts as; the formulas of substances, the relative solubility of salts, the relative volatility of various solid or liquid substances and the relative strength of weak electrolytes.

3. *Properties of sodium ion.* The chemistry of Na^+ is extremely simple and may be summarized by saying that, at ordinary temperatures, with a few uncommon exceptions, all of its compounds are non-volatile, readily soluble and strong electrolytes.

4. *Flame test for sodium. Experiment.* Clean an iron wire by dipping it into dilute HCl solution in a test-tube and holding the wire in the flame until it gives only a faint yellow color. (*Note.* Do not contaminate your HCl solution by dipping the iron wire into the bottle.) Try the flame test with a solid sodium salt, the laboratory solution of a sodium salt, a very dilute solution and distilled water. The test is extremely delicate and substances which do not contain measurable amounts of sodium usually give a slight yellow color for a short time. Therefore, before concluding that sodium is present in an "unknown" it is well to make comparative tests with known solutions (1) free from sodium and (2) the same solution containing a small amount of sodium salt. Such experiments are called *blank tests*.

5. *Properties of potassium ion.* What is the relation of K and Na in the Periodic System? Potassium ion resembles sodium ion very closely. One difference, however, is the precipitation of potassium cobaltinitrite when cobaltinitrite ion, $\text{Co}(\text{NO}_2)_6^{--}$ is added to a solution containing K^+ . *Experiments.* To

5 cc. of a dilute, neutral solution of a potassium salt add a few drops of acetic acid and 2 to 5 cc. of the sodium cobaltinitrite reagent; let the mixture stand 10 minutes.

6. *Flame test for potassium.* Try the flame test with solid KCl, KCl solution, KCl solution containing a small amount of NaCl, NaCl solution, and NaCl solution containing a small amount of KCl. Use the blue glasses to shut off the yellow color of the sodium flame and practice until the presence or absence of both potassium and sodium can be determined. *Note.* Since the flame test depends upon the amount of solid present it is well to concentrate a dilute solution by evaporation before making the test. Chlorides give more satisfactory flame tests than sulfates or oxides, which is due to the relatively greater volatility of the chlorides.

7. *Properties of ammonium ion.* The ammonium ion resembles sodium ion and potassium ion in that with few exceptions its compounds are soluble, strong electrolytes. Like the potassium ion it forms a precipitate with $\text{Co}(\text{NO}_2)_6^{---}$. Repeat the *experiment* in Paragraph 4, using NH_4^+ instead of K^+ . Ammonium compounds give no flame test. The chemistry of NH_4^+ is made somewhat more complicated by the fact that NH_4OH not only is a weak base, but is decomposed easily into NH_3 and H_2O . NH_3 , ammonia, enters into many reactions which will be considered in later Assignments. *Experiment.* Note the odor of the 6 N NH_4OH laboratory reagent; prepare some dilute solutions of NH_4OH , e. g., 0.1 N etc., heat gently about 10 cc. of each solution (moving the test-tube back and forth through the flame) and note the odor from time to time; decide what is the most dilute solution you can detect by means of the odor of NH_3 gas. Determine by experiment whether you can detect the odor of NH_3 gas when a solution of NH_4Cl or $(\text{NH}_4)_2\text{SO}_4$ is boiled. Suggest a *method of testing for ammonium ion* based on the formation first of NH_4OH in the solution and then of NH_3 gas. Write equations. *Experiment.* Try your method with a dilute solution of an ammonium salt.

8. *Volatility of ammonium compounds.* Ammonium compounds are much more volatile than those of sodium and potassium. *Experiment.* Evaporate a small amount of (a) NH_4Cl solution and (b) a mixture of NH_4Cl and KCl solutions to dryness in a porcelain dish and heat until fumes are no longer given off. Suggest a method other than the flame test of determining the presence of K^+ in a solution which contains both K^+ and NH_4^+ .

9. *Properties of H^+ and OH^- .* Aside from the tendency of H^+ and OH^- to unite with each other to form water each of these ions reacts with many other ions to form weak electrolytes. We have already noted the reaction between H^+ and Ac^- and OH^- and NH_4^+ . Acids are more volatile than their salts: the relative volatility of the common acids will be considered in Assignment 34. The OH^- also forms precipitates with many metallic ions. *Question.* How would you test for (and estimate the concentration of) H^+ or OH^- in an unknown solution?

10. Although the ions NO_3^- , Cl^- and SO_4^{--} will not be considered in detail in this Assignment, certain of their reactions will be studied in order that their presence in solutions may be detected. All nitrates are soluble, but a few chlorides and sulfates are sparingly soluble.

11. *Test for chloride ion.* *Experiment.* To 1 cc. portions of solutions of NaCl, $\text{Ba}(\text{OH})_2$, Na_2CO_3 and Na_2SO_4 add 10 cc. water, shake and add a few drops of AgNO_3 solution. In each case, record your observations, noting the color of the precipitates. Now add HNO_3 until each solution is acid. From your results state how you would test an unknown solution for chloride ion. *Note.* $\text{Ba}(\text{OH})_2$ was used instead of NaOH because Cl^- is usually present in the laboratory NaOH solutions. *Experiment.* Test a dilute solution of your NaOH for Cl^- .

12. *Test for Sulfate ion. Experiment.* To dilute solutions of NaCl, NaOH, Na_2CO_3 and Na_2SO_4 add a few drops of $\text{Ba}(\text{NO}_3)_2$ solution. Now add HNO_3 until each solution is distinctly acid. From your results state how you would test an unknown solution for SO_4^{--} .

13. *Test for nitrate ion.* Try the following experiment with a solution which contains nitrate ion and with one free from nitrate ion, first acidifying with 6 *N* H_2SO_4 if the solution is alkaline. To about 2 cc. of the solution to be tested for nitrate ion add in excess a solution of ferrous sulfate, FeSO_4 (or of ferrous ammonium sulfate,—a *double salt* of ferrous sulfate and ammonium sulfate), filter if there is a precipitate, hold the test tube in a slanting position, and pour carefully down the side of the test-tube (from a small beaker) 2 or 3 cc. concentrated sulfuric acid. The concentrated acid sinks to the bottom of the tube and a dark brown ring forms on its surface when nitrate is present. *Note.* The brown substance decomposes rapidly when the mixture is hot. If the result of the test is negative and the test-tube feels hot to the hand (owing to the heat liberated when the concentrated H_2SO_4 mixes with the solution), repeat the test more carefully.

14. Make up solutions of various concentrations of Cl^- and try *experiments* to determine if your test can be used to decide whether the concentration of Cl^- is large or small. Repeat for the nitrate and sulfate tests.

15. *Analyses Nos. A and B.* Analyze the *unknowns* for the four positive and four negative constituents considered in this Assignment. Try to distinguish between large amounts, small amounts, and traces.

16. *Problems.* (1) What is the valence of each of the 4 positive and 4 negative ions considered in this Assignment? Write the formulas of the sixteen possible compounds, each of which contains one positive and one negative constituent (cf. Hildebrand, pages 90-91). Name each of the sixteen substances, state whether it is a solid, liquid or gas at room temperature, whether it is readily soluble in water or not, and whether it is a strong or weak electrolyte.

(2) What is the valence of sodium in (a) solid sodium sulfate, (b) metallic sodium?

(3) A solid unknown was dissolved in water and the solution was found to give distinct tests for Na^+ , K^+ , Cl^- and SO_4^{--} . What conclusions can you draw with regard to the nature of the solid salts in the original mixture?

(4) Outline experiments to decide whether or not each of the following contains the impurity named:

- (a) Barium chloride impurity in the barium hydroxide solution.
- (b) Potassium chloride in solid sodium chloride.
- (c) Potassium chloride in solid ammonium chloride.
- (d) Ammonium chloride in solid potassium chloride.
- (e) Sodium nitrate in solid sodium sulfate.

(5) In each of the following it is assumed that two solutions are mixed each of which contains one of the substances at moderate concentration, say 0.1 *M*. Mark the cases in which no reaction takes place. In the others write the equation for the reaction. In (a), (b), (c) state what solutions you would use in the experiment.

- | | | |
|---|---|--|
| (a) Ac^- and Cl^- | (d) NH_4OH and K^+ | (g) K^+ and Ac^- |
| (b) NH_4^+ and Na^+ | (e) H^+ and Ac^- | (h) Ag^+ and Cl^- |
| (c) NH_4OH and H^+ | (f) K^+ and OH^- | (i) Ba^{++} and Cl^- |

ASSIGNMENT 32

CALCIUM ION

References. Hildebrand, pages 175-179, 192-193 and 207.

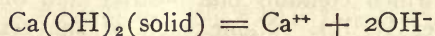
1. In Assignment 32 we shall study the chemistry of metallic calcium and of calcium ion, including its formation from metallic calcium. We shall find that certain compounds of this element differ from the corresponding compounds of sodium, potassium, and ammonium in that they dissolve to a much smaller extent in water; and we shall study the equilibrium between these solids and their saturated solutions.

2. *Note.* In future write equations for all reactions.

3. Obtain from the office a piece of metallic calcium. Describe its properties as far as you can observe them by physical examination. In what respects does calcium show the physical properties of a metal?

4. *Reaction between calcium and water. Experiment.* Drop the calcium into about 20 cc. of water. Stir the mixture and warm it gently until the metal has disappeared. Test the solution for OH^- . What reaction has occurred? The white solid formed, calcium hydroxide, $\text{Ca}(\text{OH})_2$, is a strong base but only moderately soluble in water. Cork the test-tube and save the mixture for use in a later experiment. *Question.* Name two other metals that react readily with water. What reactions occur?

5. *Calcium hydroxide.* If solid calcium hydroxide is shaken with water until a saturated solution is obtained an equilibrium between solid $\text{Ca}(\text{OH})_2$ and the ions Ca^{++} and OH^- is established. The equation for the reaction that has taken place is



The solubility of $\text{Ca}(\text{OH})_2$ at room temperature is 0.02 mols per liter. *Questions* What is the concentration of calcium ion, of hydroxide ion, (1) in mols per liter, and (2) in equivalents per liter? Is the reaction just considered reversible? What solutions would you mix in order to prepare solid $\text{Ca}(\text{OH})_2$? Try the *experiment*.

6. Which contains the larger concentration of OH^- , a saturated solution of $\text{Ca}(\text{OH})_2$ or 1 N NH_4OH (see Assignment 23)? State what you think will happen when a dilute solution of calcium chloride is made alkaline with ammonium hydroxide. Try the *experiment*. Explain the result if your prediction was incorrect.

7. State what would happen if a solution of calcium hydroxide were treated with (1) hydrochloric acid, (2) ammonium chloride. Predict what would happen if solid $\text{Ca}(\text{OH})_2$ were also present in each case. *Experiment.* Test your answers by experiments with portions of the mixture prepared in Paragraph 4. *Questions.* How would you use calcium hydroxide to test a solution for ammonium ion?

8. *Calcium carbonate.* The solubility of CaCO_3 in water at room temperature is very small, viz., 0.00013 mols per liter. *Question.* What is the concentration of calcium ion, of carbonate ion, in this saturated solution, (1) in mols per liter, (2) in equivalents per liter? What solutions would you mix in order to form a precipitate of calcium carbonate? Try the *experiment*. Write the simplest ionic equation for the reaction. Continue the experiment with very dilute solutions of a calcium salt in order to determine if this reaction can be used as a delicate *test for calcium ion*. In the more dilute solutions, if a precipitate does not form at once, heat to boiling and let stand 10 minutes. If the liquid is turbid compared with water a precipitate has formed.

9. *Experiment.* Dilute 5 cc. N CaCl_2 with about 100 cc. water, add about 8cc. N Na_2CO_3 solution, heat the mixture to boiling, filter, wash the precipitate and reject the wash water. Consider what substances may be present in the filtrate. Test for chloride ion and for calcium ion. Which reagent was present in excess, calcium chloride, or sodium carbonate?

10. *Experiment.* Treat a portion of the CaCO_3 precipitate with hydrochloric acid solution. Repeat the experiment with nitric acid. The gas given off is carbon dioxide, CO_2 . What substances are present in the final solution in each case after the solution has been boiled to expel the CO_2 ? *Note.* CO_2 is moderately soluble in cold water and the solution contains carbonic acid, H_2CO_3 , which is a weak acid. CO_2 gas will not be evolved until the concentration of carbonic acid in the solution becomes sufficiently high. *Questions.* How is the equilibrium between solid CaCO_3 and its ions disturbed by the addition of a strong acid? What is the analogy between this example and the action of an acid on solid $\text{Ca}(\text{OH})_2$, and on solid silver acetate? What is the reason for the difference between these results and that obtained when dilute nitric acid is added to silver chloride or barium sulfate?

11. *Test for carbonate. Experiment.* Fit a test-tube with stopper and delivery tube. Place a small amount of any carbonate in the tube and add a few cc. of 6 N H_2SO_4 . Insert the stopper and pass the gas given off into a clear solution of $\text{Ca}(\text{OH})_2$.* If only a small amount of carbonate is present the CO_2 will not pass over into the $\text{Ca}(\text{OH})_2$ solution. A satisfactory test may be obtained in this case by placing the test-tube in a beaker of boiling water, or by adding a small piece of zinc to the cold mixture in the test-tube. The CO_2 is carried over with the dissolved air and steam in the first method, and with the hydrogen gas in the second.

12. *Calcium oxalate. Experiment.* Prepare some CaC_2O_4 by treating a solution containing calcium ion with ammonium oxalate solution. Test the action of excess of a strong acid, as HCl or HNO_3 on CaC_2O_4 . *Question.* Is oxalic acid, $\text{H}_2\text{C}_2\text{O}_4$, a weak or a strong acid?

13. *Experiment.* Determine if the precipitation of CaC_2O_4 is a delicate test for calcium by treating very dilute solutions of Ca^{++} with ammonium oxalate solution and a little ammonium hydroxide (to make sure that the mixture is not acid). Observe the same precautions as in the test for calcium by means of CO_3^{--} . *Note.* The solubility of calcium oxalate in water is even less than that of calcium carbonate.

14. *Calcium sulfate. Experiment.* To 10 cc. normal CaCl_2 solution add 2 cc. 6 normal H_2SO_4 . If no precipitate appears at once, heat the solution gently, and let it stand. Filter. Test a portion of the filtrate for Ca^{++} by adding NH_4OH until the solution is no longer acid, and then $(\text{NH}_4)_2\text{CO}_3$ solution, and warming the mixture. Test another portion for SO_4^{--} . What conclusion do you draw with regard to the solubility of CaSO_4 in water? Which is the less soluble, (1) CaSO_4 or CaCO_3 , (2) CaSO_4 or BaSO_4 ?

15. Predict what will take place when solid CaSO_4 is heated with excess Na_2CO_3 solution? *Experiment.* Test your prediction by boiling some solid CaSO_4 with normal Na_2CO_3 solution. Test the filtrate for SO_4^{--} . Wash the precipitate with water, and test it for carbonate.

16. *Experiment.* Test whether the reverse reaction will take place, by heating solid CaCO_3 with sodium sulfate solution, filtering and testing the precipitate and filtrate.

*Instead of $\text{Ca}(\text{OH})_2$ solution, $\text{Ba}(\text{OH})_2$ solution may be used; BaCO_3 , like CaCO_3 is a difficultly soluble substance.

17. *Flame test for calcium. Experiment.* Determine whether calcium salts give a characteristic flame test. Can you distinguish the flame with a calcium salt from that with sodium or potassium salts?

18. *Note.* The solubilities of many common salts at 18° are listed on the inside cover page of Alexander Smith's text-book. Do not try to remember the actual solubilities, but make lists of the readily soluble and difficultly soluble salts of each metal studied and memorize these lists. Arrange the compounds of calcium according to their solubilities in water, distinguishing readily soluble, moderately soluble, and difficultly soluble substances. Point out the compounds which are much more soluble in dilute hydrochloric or nitric acids than in water.

19. Give as many methods as you can of testing for Ca^{++} in a solution which is known to contain H^{+} , Na^{+} , K^{+} and NH_4^{+} .

20. *Problems.* (1) What is the minimum volume of water needed at 18° to dissolve 1 gram of calcium carbonate?

(2) Can the following substances be present at moderate concentrations in the same solution? If not, what is formed?

(a) H^{+} and NO_3^{-}

(e) H^{+} and $\text{C}_2\text{O}_4^{--}$

(b) H^{+} and OH^{-}

(f) Ca^{++} and CO_3^{--}

(c) H^{+} and SO_4^{--}

(g) Ca^{++} and NO_3^{-}

(d) H^{+} and CO_3^{--}

(h) Ca^{++} and NH_4OH

(3) How would you prepare:

(a) Solid CaCO_3 from solid $\text{Ca}(\text{OH})_2$?

(b) Solid CaSO_4 from solid CaCO_3 ?

(c) Solid CaC_2O_4 from solid CaSO_4 ?

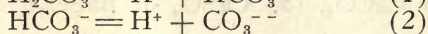
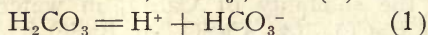
Write equations for all reactions, and point out what equilibria are involved.

(4) What is the position of calcium in the Periodic System? Name the elements in the alkaline earth group. Write a brief note illustrating gradations of properties in this group, after examining the table given by Hildebrand on page 268.

ASSIGNMENT 33

CARBONATE ION, BICARBONATE ION, AND CARBONIC ACID

1. This assignment, in which we shall study the chemistry of carbonic acid and its ions, is introduced, not only because this subject is an extremely important one, but also because it serves to illustrate how a large number of facts can be correlated when the equilibria involved in a few simple, reversible reactions are understood. Carbonic acid, H_2CO_3 , is a *weak, dibasic acid*; and, like other weak acids which contain more than one acidic hydrogen in the molecule, it ionizes in steps, to form (1) bicarbonate ion, HCO_3^{-} , and (2) carbonate ion, CO_3^{--} , thus:



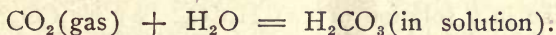
In order to understand what happens in the various reactions considered, it is necessary to know the relative concentrations, in the initial and final solutions, of the substances involved in these two rapid reversible reactions. Our problem, then, is to determine how the concentrations of H^{+} (or OH^{-}), H_2CO_3 , HCO_3^{-} and CO_3^{--} at equilibrium in a solution vary as the experimental conditions are changed.

2. Obtain at the office a large and small two-holed rubber stopper, two pieces of rubber tubing and a thistle tube for use in the experiment in paragraph 3 and a hard glass test-tube for use in the experiment in Paragraph 12.

3. *Preparation and properties of carbon dioxide. Experiment.* Make a carbon dioxide generator by fitting your half-liter flask with the thistle tube (passing through the stopper nearly to the bottom of the flask), and an outlet tube bent at right angles. Make a wash bottle for washing the CO_2 gas by equipping a small flask with an entry tube extending nearly to the bottom of the flask, and a delivery tube. Fill the small flask about half full of water. Place in the generator a few lumps (about 5 grams) of limestone, cover with water, and add hydrochloric acid, a little at a time, through the thistle tube.

Note the color and the odor of the gas. Calculate from the molecular weights the relative densities of carbon dioxide and oxygen, and of carbon dioxide and nitrogen, at the same temperature and pressure. *Question.* Is carbon dioxide denser or lighter than air? *Experiment.* Collect some carbon dioxide in a test-tube by displacement of air; and determine if it is inflammable, and if it supports combustion.

4. Suggest an experiment to prove that carbon dioxide is moderately soluble in water at room temperature. Try the *experiment*. When CO_2 dissolves in water the reaction is



Prove by an *experiment* that the reverse reaction can take place. Under what conditions is there an equilibrium? *Note.* At room temperature a solution in equilibrium with CO_2 gas at 1 atmosphere pressure contains about 0.04 mols H_2CO_3 in 1 liter. *Question.* How is this equilibrium altered by an increase of temperature?

5. We shall now consider what the principal substances are in a saturated carbonic acid solution. *Experiment.* Prepare a small quantity of nearly saturated solution of CO_2 and test it with the indicators, phenolphthalein, litmus, methyl orange, and methyl violet; for comparison repeat indicator tests with water and with an acid solution of known H^+ concentration. What conclusion can you draw with regard to the concentration of H^+ in the saturated CO_2 solution? *Note.* The concentration of H^+ in this solution has been determined by other methods to be about $0.0001\text{ }N$ ($10^{-4}N$). From this value for the concentration of H^+ , the concentration of OH^- in the same solution can be calculated to be $10^{-10}\text{ }N$; explain how this calculation is made, cf. Hildebrand, page 180.

6. *Experiment.* Test the action of carbonic acid on Ca^{++} by passing CO_2 gas into a dilute solution of CaCl_2 . What conclusion can you draw with regard to the concentration of CO_3^{--} in carbonic acid solution? The concentration of CO_3^{--} in the $0.04\text{ }M$ H_2CO_3 solution has been found by other methods to be of the same order of magnitude as that of OH^- . *Questions.* Making use of the fact that the only ions in this solution are produced by the ionization of H_2CO_3 (and H_2O), what conclusion can you draw with regard to the extent to which each of the reactions (1) and (2), Paragraph 1, has taken place in a solution of carbonic acid? What is the approximate concentration of HCO_3^- in the $0.04\text{ }M$ H_2CO_3 solution? List the substances present in this solution (a) at moderate concentration, (b) at small concentration (two substances), and (c) at extremely small concentration (two substances).

7. *The neutralization of carbonic acid.* When NaOH solution is added gradually to a carbonic acid solution the neutralization of H_2CO_3 takes place in steps corresponding to the two steps in the dissociation of H_2CO_3 . The main reaction for the first step in the neutralization is



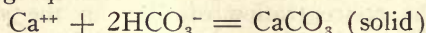
and the solution made from equal molal quantities of H_2CO_3 and NaOH is a sodium bicarbonate solution. The second step in the neutralization of H_2CO_3 is

$$\text{HCO}_3^- + \text{OH}^- = \text{H}_2\text{O} + \text{CO}_3^{--}$$

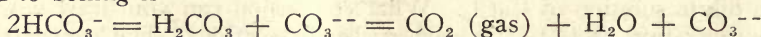
This is the reaction for the neutralization of HCO_3^- by a strong base, and was considered in Assignment 25.

8. *Substances present in a solution of sodium carbonate.* Review your notes, Assignment 25, on the relative concentrations of CO_3^{--} , HCO_3^- and OH^- in a 0.5 M Na_2CO_3 solution; and calculate the concentration of H^+ in this solution. The concentration of H_2CO_3 in this solution is also extremely small, but of course is greater than the concentration of H^+ . *Questions.* How would you prepare 1 mol of solid Na_2CO_3 from 1 mol of NaHCO_3 , and also from 1 mol of H_2CO_3 ? What quantity of NaOH would be required in each case? List the substances which are present in a solution of Na_2CO_3 , (a) at moderate (or high) concentration, (b) at relatively small concentration (two substances), and (c) at extremely small concentration (two substances).

9. *Substances present in a solution of sodium bicarbonate.* From the fact that HCO_3^- is a weak acid, what would you expect to be the principal substances in a solution of NaHCO_3 ? Noting that the substance HCO_3^- is intermediate in composition between H_2CO_3 and CO_3^{--} , and considering the equilibria involved, would you expect the concentration of CO_3^{--} in a solution of NaHCO_3 to be greater or less than in a solution of (a) H_2CO_3 , (b) Na_2CO_3 ? The following experiment, on the precipitation of CaCO_3 by NaHCO_3 solution at room temperature, furnishes evidence with regard to the concentration of CO_3^{--} in this solution, (but it should be remembered that more CaCO_3 is precipitated than corresponds to the actual concentration of the CO_3^{--} since on account of the displacement of equilibrium some more CO_3^{--} forms as the CaCO_3 is precipitated). *Experiment.* To 10 cc. M NaHCO_3 in a flask add about 50 cc. water, and 10 cc. N CaCl_2 ; shake the mixture. Filter and note the amount of the CaCO_3 precipitate. Compare the result with that obtained in the experiment with Ca^{++} and H_2CO_3 , Paragraph 6. Repeat the experiment using 10 cc. N (0.5 M) Na_2CO_3 instead of 10 cc M NaHCO_3 . Heat the two filtrates to boiling, and test the gas evolved in the NaHCO_3 experiment by passing it into a clear solution of $\text{Ca}(\text{OH})_2$ or $\text{Ba}(\text{OH})_2$ (cf. Assignment 32, Paragraph 11). Compare the amount of the precipitate now obtained with that formed in the cold solution. Complete the following equation:



and suggest an explanation for the shifting of the equilibrium when the mixture is heated to boiling. The reaction that takes place when a solution of NaHCO_3 is heated to boiling is



Questions. How will the concentrations of H_2CO_3 and CO_3^{--} in a NaHCO_3 solution be changed (1) when the solution is boiled, and (2) when CaCl_2 solution is added at room temperature? What conclusions can you draw with regard to the relative concentrations of HCO_3^- , and H_2CO_3 and CO_3^{--} in a freshly prepared, cold solution of NaHCO_3 ?

10. *Experiment.* Test a freshly prepared, approximately molal solution of NaHCO_3 with litmus and with phenolphthalein and estimate approximately the concentration of OH^- and H^+ in the solution. Repeat the experiment with a solution which has been heated to boiling, or which has been allowed to stand in the laboratory for several days. From your results in Paragraphs 9 and 10 state which substances are present in a pure NaHCO_3 solution, (a) at moderate (or high) concentration, (b) at relatively small concentration, (two substances) and (c) at still smaller concentration (two substances).

11. Summarize in tabular form the lists referred to in the last sentence of each of the three Paragraphs, 6, 10 and 8, arranging the columns in the order H_2CO_3 , NaHCO_3 and Na_2CO_3 . Note the regular change in the concentration of each substance, e. g. H_2CO_3 , when the three solutions are considered in this

order. If the arrangement of the various substances in your table is not symmetrical you have probably made some mistake. *Question.* What is the equation for the main reaction when 0.1 mol of strong acid is added to (a) 0.1 mol Na_2CO_3 , and (b) 0.05 mol Na_2CO_3 ?

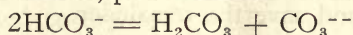
12. *The decomposition of solid sodium bicarbonate. Experiment.* Place about 1 gram NaHCO_3 in a hard-glass test-tube and lead the delivery tube into a solution of $\text{Ba}(\text{OH})_2$, or of CaCl_2 and NH_4OH . Heat the tube until no more gas is given off, remove the delivery tube from the solution, and allow the hard-glass tube to cool. What is the evidence that CO_2 was formed? That water was formed? What must the residue be if H_2O and CO_2 are formed in equimolal quantities? (This experiment may be performed quantitatively by weighing the hard-glass tube (1) empty, (2) with NaHCO_3 , and (3) with the residue.)

Experiment. Continued. Clean the delivery tube and lead it into a fresh solution of $\text{Ba}(\text{OH})_2$. Pour water carefully into the hard-glass tube until it is half full, but do not stir the mixture. Add 2 cc. 6 *N* HCl , and at once insert the stopper. What is the gas evolved? Warm the mixture slowly by placing the hard-glass tube in a beaker of water and heating the latter. *Questions.* If the gas volumes had been measured, what would have been the ratio of the volumes in the two parts of the experiment? If all the CO_2 evolved had been converted into BaCO_3 , what would have been the relative amounts obtained in the two parts of the experiment?

13. *Reaction between an acid and the negative ion of a weaker acid.* Give examples of the action of a strong acid on a solution of the salt of a weak acid. *Experiment.* Determine the action of dilute acetic acid on NaHCO_3 . Which is the stronger acid, HAc or H_2CO_3 ? Taking into consideration the fact that HCO_3^- , the negative ion of H_2CO_3 , is also a weak acid (whose ions are H^+ and CO_3^{--}), and the additional fact that H_2CO_3 is a stronger acid than HCO_3^- , predict what will happen when H_2CO_3 is introduced into a solution of a carbonate.

14. *Experiment.* Test your answer to the last question by placing a small amount of freshly precipitated CaCO_3 in about 100 cc. water and saturating the mixture with CO_2 . Filter off any CaCO_3 that remains and heat the filtrate to boiling.

15. Summarize all the evidence, presented in this Assignment that the reaction



is reversible, noting especially the experimental conditions under which the reaction will proceed almost completely, (a) as written, and (b) in the reverse direction. *Question.* Which solution would be more alkaline at room temperature (on account of hydrolysis), a molal solution of a salt of a weak monobasic acid of the same strength as H_2CO_3 , or a molal solution of NaHCO_3 ? Give your reasoning.

16. *Problems.* (1) Can the following substances be present at moderate concentrations in the same solution? If not, what is formed?

- | | |
|--|---|
| (a) H_2CO_3 and Ca^{++} | (f) HCO_3^- and H^+ |
| (b) H_2CO_3 and OH^- | (g) HCO_3^- and OH^- |
| (c) H_2CO_3 and CO_3^{--} | (h) HCO_3^- and CO_3^{--} |
| (d) H_2CO_3 and HCO_3^- | (i) CO_3^{--} and OH^- |
| (e) H_2CO_3 and H^+ | |

(2) What weight of Na_2CO_3 can be obtained from 8.4 g. NaHCO_3 , (a) by heating, and (b) by treating the bicarbonate with NaOH solution? What is the least volume of *N* NaOH that can be used in (b)?

(3) What volume of CO_2 at standard conditions can be obtained from 8.4 g. NaHCO_3 , (a) by heating, and (b) by treating the bicarbonate with HCl solution? What is the least volume of N HCl that can be used in (b)?

(4) When a current of CO_2 is passed into a solution of $\text{Ca}(\text{OH})_2$ a precipitate is observed to form, and then dissolve. If the final solution is now heated to boiling, a precipitate again appears. State what has happened in this experiment, and write an equation for the main reaction in each of these stages.

ASSIGNMENT 34

SULPHATES, CHLORIDES AND NITRATES OF COPPER AND ZINC

1. In Assignment 34 and the four following Assignments we shall study the chemistry of copper ion, Cu^{++} , silver ion, Ag^+ , and zinc ion, Zn^{++} . We shall first devote our attention to the common soluble salts, and to the method of transforming one salt into another; and then we shall study the sparingly soluble compounds, the methods of dissolving them, and the equilibria involved. The same method of treatment will be used later in studying the chemistry of ions of other metals, and many of the results now obtained in studying copper, silver and zinc are also true for other metals. Read again Paragraph 2, Assignment 31.

2. *Solubility of nitrates, acetates, chlorides and sulfates of metals.* The nitrates and acetates of all metals are soluble in water and this is also true for nearly all the chlorides and sulfates. *Question.* Give an example of a difficultly soluble chloride and of a difficultly soluble sulfate. Give the formulas of the nitrates, acetates, chlorides and sulfates of copper, silver and zinc.

3. *Preparation of sulfates from nitrates and chlorides. Experiment.* Test the relative volatility of HCl , HNO_3 and H_2SO_4 by evaporating a few drops of a concentrated solution of each of these acids in a casserole (out of doors or in a fume closet). Cf. Hildebrand, pages 173-175. Suggest a method of preparing solid copper sulfate from copper nitrate based on the difference in volatility of HNO_3 and H_2SO_4 . *Experiment.* Try your method with 15 cc. of the laboratory solution of copper nitrate. Recrystallize the copper sulfate by mixing the residue, after it is cold, with 2 or 3 cc. water, heating the mixture to boiling and letting it cool slowly. Wash the crystals with a very little water, test a small portion for NO_3^- , and save the remainder.

4. Suggest a similar method for the preparation of solid zinc sulfate from zinc chloride. How would you test whether the final product is free from chloride?

5. The problem of preparing a soluble chloride or nitrate from a soluble sulfate will be considered in the following Assignment.

6. *Conversion of soluble chlorides into nitrates, and nitrates into chlorides. Experiment.* Mix 2 cc. concentrated HNO_3 solution and 6 cc. concentrated HCl solution, and let the mixture stand. Evaporate a few drops of the solution to dryness (out of doors or in a fume closet) and note if there is a residue. The gradual deepening of the color of the solution at room temperature proves not only that a reaction is taking place but that this reaction is not a rapid one. *Questions.* How would the speed of the reaction be altered (a) by raising the temperature, and (b) by using less concentrated acids? *Note.* Although this reaction does not take place in a dilute solution which contains H^+ , Cl^- and NO_3^- , it can be made to do so by concentrating the solution by evaporation to a small volume. Since both Cl^- and NO_3^- are used up in this reaction and the products are volatile, we can make use of this reaction (1) to remove Cl^- from a solution by heating with excess of concentrated HNO_3 , or (2) to remove

NO_3^- from a solution by heating with excess of concentrated HCl . *Question.* If excess of concentrated HNO_3 is added to a small amount of NaCl and the mixture evaporated just to dryness, what would you expect the solid residue to be. *Note.* The mixture of concentrated HNO_3 and HCl is called *aqua regia*, and the reaction that takes place is $\text{NO}_3^- + 3 \text{Cl}^- + 4\text{H}^+ = \text{NOCl} + \text{Cl}_2 + \text{H}_2\text{O}$.

7. *Experiment.* To about 0.2 g. copper chloride (or 2 cc. N ZnCl_2 solution) in a casserole, add 3 cc. concentrated HNO_3 and stir; add one or two drops of this mixture to 10 cc. water, test this solution for Cl^- and set it aside for comparison with later results. Evaporate the mixture of the chloride and concentrated HNO_3 just to dryness (out of doors or in a fume closet), add 5 cc. concentrated HNO_3 being careful to dissolve any solid on the side of the dish, and test one or two drops of the solution for Cl^- as before. Again evaporate the mixture just to dryness, and test a portion of the residue for chloride. *Questions.* What is the final solid residue? What conclusion can you draw from a comparison of the amounts of the AgCl precipitates in your three tests? Does this experiment furnish any evidence that the reaction is slow, even at a temperature in the neighborhood of 100° , when the concentration of one of the reacting substances is small?

8. How would you convert copper nitrate, or zinc nitrate, into the chloride?

9. *Treatment of silver chloride with hot concentrated nitric acid and sulfuric acid. Experiment.* Prepare some silver chloride, and wash it with dilute HCl and then with water. Place a small amount of the silver chloride in a porcelain dish, and 3 or 4 cc. concentrated HNO_3 , evaporate the mixture to dryness. Add a little water and test the solution for Ag^+ . Repeat the experiment with the residue. Compare the result with that in the experiment in Paragraph 7, and state how the speed of the reaction between Cl^- and NO_3^- in acid solution depends on the concentration of Cl^- .

10. Test the action of hot concentrated H_2SO_4 on silver chloride by heating for several minutes a small amount of the salt with 3 or 4 cc. of the acid in a porcelain dish covered with a watch glass. Set the dish aside until it is cool, pour the mixture into water, and test the solution for Ag^+ . *Note.* The chloride is expelled as HCl gas in this experiment, but since the temperature may have exceeded 300° it is not surprising that the result is different from that obtained in the experiment with AgCl and concentrated HNO_3 .

11. *Problems.* (1) What will be the solid residue when each of the following solutions is evaporated to dryness?

(a) A solution which contains Ag^+ , H^+ and NO_3^- .

(b) A solution which contains Cu^{++} and NO_3^- at small concentrations and H^+ and SO_4^{--} at large concentrations.

(c) A solution which contains Cu^{++} and NO_3^- at large concentrations and H^+ and SO_4^{--} at small concentrations.

(d) A solution of zinc sulfate to which nitric acid has been added.

(2) How would you prepare solid silver sulfate from (a) solid silver nitrate, (b) solid silver acetate?

(3) When solid copper sulfate is prepared by crystallization from an aqueous solution it contains *water of crystallization* and its formula is $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. When this blue substance is heated, white anhydrous CuSO_4 is finally obtained. Write the equation. The reverse reaction takes place when air saturated with water vapor is passed over the anhydrous salt at room temperature. If a vessel containing $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ were evacuated for a few minutes and then closed, what substances would be present in the closed vessel? What reason do you have for the conclusion that the pressure of water vapor in the vessel at room temperature must be less than the partial pressure of water vapor at the same

temperature? How would the pressure in the vessel be altered by raising the temperature? Give two other examples of a reversible reaction in which one solid substance dissociates into another solid and a gas, and in each case give an approximate value for the equilibrium pressure at some definite temperature. (Refer to the lectures on the dissociation of calcium carbonate and calcium hydroxide when heated.)

ASSIGNMENT 35

HYDROXIDES OF COPPER, SILVER AND ZINC

References. Hildebrand, Chapter V pages 72-73, 80-82; Chapter XIII pages 194-195.

1, We have learned from the laboratory work and the lectures that the hydroxides of sodium, potassium and the other alkali metals, and ammonium hydroxide are readily soluble in water, and that the hydroxides of barium, strontium and calcium are moderately soluble (with the solubility decreasing rather rapidly in the order named). The hydroxides of all other metals are difficulty soluble in water.

2. *Cupric hydroxide.* State what solutions you would mix to prepare $\text{Cu}(\text{OH})_2$. Point out the substances involved in the equilibrium between the solid and its saturated solution and predict what will happen when the solid is treated with HCl , HNO_3 or H_2SO_4 solution. *Experiment.* Test your answer by preparing some copper hydroxide and treating it with acids. Also determine if it dissolves in 0.5 *N* NaOH .

3. *Cupric oxide.* *Experiment.* Collect some $\text{Cu}(\text{OH})_2$ on a filter and wash it once with water. Mix some of the $\text{Cu}(\text{OH})_2$ with water and heat the mixture to boiling. Place the remainder of the $\text{Cu}(\text{OH})_2$ in a procelain dish and heat gently. Cupric oxide has formed. Does the reverse reaction between CuO and H_2O take place at room temperature? Predict what will happen when NaOH solution is added to a solution of $\text{Cu}(\text{NO}_3)_2$ at 100° , and test your answer. Test the action of HCl , HNO_3 or H_2SO_4 solution on CuO . *Question.* How would you prepare solid CuCl_2 from $\text{Cu}(\text{OH})_2$ or CuO ?

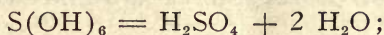
4. *Silver oxide.* *Experiment.* To 10 cc. 0.1 *N* AgNO_3 solution add NaOH solution slowly until, after shaking, the solution reacts strongly alkaline to litmus. Silver oxide, Ag_2O , is formed. Filter, acidify the filtrate with HNO_3 and test it for Ag^+ . Write the equation for the reaction between Ag^+ and OH^- to form Ag_2O . Point out the substances involved in the equilibrium between the solid substance and its saturated solution, and predict what will happen when the solid substance is treated with HNO_3 solution. Test your answer by an experiment.

5. *Relation between oxides and hydroxides of metals.* Contrast the action of water or water vapor at room temperature on calcium oxide, and on copper oxide or silver oxide. Review Problem 3, Assignment 34; and note that the reaction

Oxide of a metal (solid) + H_2O (gas) = Hydroxide of a metal (solid) takes place completely in the case of oxides of the alkali metals, as Na_2O , does not have any tendency to take place in the case of oxides of the more noble metals, as Ag_2O , and can be shown to be reversible for many oxides which are intermediate between these two extremes. (In many cases equilibrium is reached only very slowly, especially at low temperatures.) On account of this relation between oxides and hydroxides of metals, it is not surprising that oxides of metals in general are capable of neutralizing acids. *Questions.* What is anhydride of a base? Give examples. Is it always correct to say than an

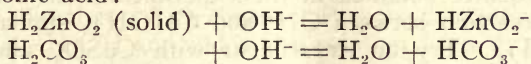
anhydride of a base will react with water to form the base? What is an *acid anhydride*? Give examples. Also give examples of reactions between an acid anhydride and a base, and between an acid anhydride and a basic anhydride.

6. Acids which contain oxygen may be considered to be related to the hydroxides of non-metals. Thus H_2SO_4 may be regarded as H_6SO_6 or $\text{S}(\text{OH})_6$ from which 2 molecules of water have been withdrawn



and the formula of phosphorous acid, H_3PO_3 , may be written $\text{P}(\text{OH})_3$. The characteristic properties of these acids, to yield negative ions containing oxygen on dissociation or neutralization, is then to be attributed to the existence of strong bonds between the non-metal and the oxygen in the compound; which is really due to the great tendency of non-metals to hold electrons firmly. On the other hand metals in compounds do not hold electrons firmly, and positive ions of metals are formed when bases or salts dissociate. However, certain elements which form a positive ion also can form a negative ion containing oxygen; the hydroxide of such an element has the properties of a base in that it can neutralize an acid, and also has the properties of an acid since it can neutralize a base: it is said to be *amphoteric*.

7. *Zinc hydroxide. Experiment.* Prepare some $\text{Zn}(\text{OH})_2$ by treating a solution containing Zn^{++} with a very small amount of NaOH . Collect the $\text{Zn}(\text{OH})_2$ on a filter, treat a portion with a strong acid, and another portion with NaOH or KOH solution. *Question.* What evidence is furnished by this experiment that zinc hydroxide is an amphoteric substance? The reaction between zinc hydroxide and excess OH^- is analogous to the first stage in the neutralization of carbonic acid:



The negative ion, HZnO_2^- , is usually *zincate ion*, though strictly speaking this name should be reserved for the ion ZnO_2^{--} . The latter substance probably forms to some extent when the concentration of OH^- is very large. Solid NaHZnO_2 has not been prepared, but Na_2ZnO_2 can be made by fusing zinc oxide with NaOH .

8. Predict what will happen when a solution of a strong acid is added slowly to sodium zincate solution. Test your answer by an *experiment*.

9. *Preparation of a nitrate or chloride from a soluble sulfate. Experiment.* Prepare a solution of copper nitrate from copper sulfate solution by precipitating copper hydroxide from a very dilute CuSO_4 solution, washing the $\text{Cu}(\text{OH})_2$ precipitate, and transforming it into the nitrate. Test the product for sulfate.

10. Suggest a second method based on the removal of the sulfate ion by means of barium ion (cf. Hildebrand, pages 207-208). Try your method, and test the copper nitrate solution for SO_4^{--} and for Ba^{++} . Which is the better method to use on a small scale in the laboratory?

11. Suggest two methods of preparing solid zinc chloride from zinc sulfate.

12. *Problems.* (1) Write equations for the action of HCl solution in excess on calcium oxide, on ferrous and ferric oxides (FeO and Fe_2O_3), on ferrous and ferric hydroxides, and on sodium zincate solution.

(2) A solution containing 0.2 mol Na_2SO_4 is mixed with a solution containing 0.1 mols $\text{Ba}(\text{NO}_3)_2$, the precipitate is removed by filtration, the wash water is run into the filtrate until the final volume of the latter is 1 liter. What substances are present in the final solution and what is the concentration of each? Suggest a method of preparing pure sodium nitrate from sodium sulfate.

(3) Give two methods of preparing CuCl_2 from CuSO_4 .

(4) Give an example of an amphoteric hydroxide other than $\text{Zn}(\text{OH})_2$, and write the equation for its reaction with (a) a strong acid, (b) a strong base.

ASSIGNMENT 36

COMPLEX IONS OF COPPER, SILVER AND ZINC WITH AMMONIA

References. Hildebrand, pages 184 and 202-205.

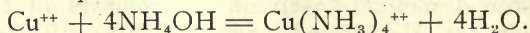
1. The ions of certain metals have the power of forming compounds with NH_3 , which are examples of "complex ions". The ammonia is supplied by adding NH_4OH solution. There is an equilibrium between the complex ion, NH_3 or NH_4OH , and the ion of the metal; and when the NH_4OH is present in excess the concentration of the ion of the metal is often very small. Some examples will be considered in the present Assignment.

2. *Experiment.* Dilute 5 cc. N CuSO_4 with 20 cc. water and add two or three drops $6 N$ NH_4OH . The precipitate is $\text{Cu}(\text{OH})_2$. *Question.* What evidence with regard to the solubility of $\text{Cu}(\text{OH})_2$ in water is furnished by this experiment? (Consider the low concentration of OH^- in NH_4OH solution and the result of the experiment in Paragraph 6, Assignment 32.

3. Continue to add the NH_4OH solution until, after shaking, the solution is clear. Observe the volume of NH_4OH used. What is the evidence that a new substance is formed? Repeat the *experiment* with the same volume of $6 N$ NaOH instead of $6 N$ NH_4OH . State the reasoning by which you may conclude that the substance obtained in the experiment with NH_4OH solution is not formed by a reaction between OH^- and $\text{Cu}(\text{OH})_2$ similar to that between OH^- and $\text{Zn}(\text{OH})_2$. Try an *experiment* with CuSO_4 solution and NH_4Cl in order to determine if Cu^{++} reacts with NH_4^+ in the same way as with NH_3 or NH_4OH .

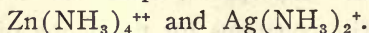
4. The new substance formed when $\text{Cu}(\text{OH})_2$ dissolves in NH_4OH solution is $\text{Cu}(\text{NH}_3)_4^{++}$. The final solution contains NH_4OH , and OH^- must be present at an appreciable concentration; it may be concluded that the concentration of Cu^{++} is extremely small, since, otherwise, $\text{Cu}(\text{OH})_2$ would precipitate. *Questions.* Which solution has the greater concentration of Cu^{++} , a saturated solution of $\text{Cu}(\text{OH})_2$ or a solution of the complex ion containing NH_4OH ? How is the equilibrium between $\text{Cu}(\text{OH})_2$ and its saturated solution affected when NH_4OH is added?

5. The equation for the main reaction when a solution of a copper salt is treated with excess NH_4OH is



A simple method of demonstrating that the reverse reaction will take place is to remove the NH_4OH . Suggest two methods of doing this and try your methods.

6. Zinc and silver also form complex ions with ammonia,



Experiment. To a dilute solution of ZnSO_4 add NH_4OH solution drop by drop, shaking the mixture after each addition of NH_4OH ; when some but not all of the $\text{Zn}(\text{OH})_2$ has dissolved test the solution with trinitrobenzol to determine approximately the OH^- concentration. Repeat the *experiment*, using NaOH instead of NH_4OH , and note again the OH^- concentration in the solution when $\text{Zn}(\text{OH})_2$ is partly but not completely dissolved. *Question.* From a comparison of the OH^- concentration at equilibrium in the two cases what conclusion can you draw with regard to the presence of zinc as a different substance in the NH_4OH and NaOH solutions?

7. *Experiment.* Prepare some silver oxide and some silver chloride, and treat each substance with NH_4OH solution. Predict what will happen when the resulting solutions are acidified with nitric acid, and test your answers by experiments.

8. Which solution would contain a greater concentration of Ag^+ , a saturated solution of silver acetate (see Assignment 24, Paragraph 5) or a solution which contains the complex ion and NH_4OH ? What then must be the action of NH_4OH solution on solid AgAc ?

9. *Questions.* When AgCl is dissolved in excess NH_4OH solution, what is the principal positive ion, and the principal negative ion, in the resulting solution? When 0.1 mols AgCl are dissolved and the final volume is 100 cc. what is the approximate concentration of each of these ions? Is the concentration of Ag^+ smaller or larger than in a saturated solution of AgCl in water?

10. When $\text{Cu}(\text{OH})_2$ is dissolved in excess NH_4OH solution what is the principal negative ion in the final solution? It is important to realize that $\text{Cu}(\text{NH}_3)_4(\text{OH})_2$, $\text{Zn}(\text{NH}_3)_4(\text{OH})_2$ and $\text{Ag}(\text{NH}_3)_2\text{OH}$ are soluble, strong bases.

11. We shall next consider the action of NH_4OH solution on silver iodide, a salt which is much less soluble in water than either silver oxide or silver chloride. Solid AgI , suspended in water, is in equilibrium with Ag^+ and I^- in the saturated solution. When NH_4OH is added some Ag^+ must react with it to form $\text{Ag}(\text{NH}_3)_2^+$, and some solid AgI must dissolve to establish again the solubility equilibrium. We can therefore predict that AgI must be more soluble in NH_4OH solution than in water, but it is not safe to predict that a large amount of it will dissolve. *Experiment.* Prepare a solution of silver oxide or silver chloride in NH_4OH and add to this solution a few drops of 0.1 *N* potassium iodide solution. In another experiment collect some solid silver iodide on a filter paper, wash it with water, and treat it with dilute NH_4OH solution. Devise and try an experiment with the solution thus prepared to determine whether an appreciable amount of AgI has dissolved.

12. Predict what will happen when silver chloride is treated with a solution of potassium iodide. Try the *experiment*.

13. The ions of the alkali metals, as Na^+ , K^+ , etc.; those of the alkaline earth metals, as Ca^{++} , Sr^{++} and Ba^{++} ; and many other positive ions do not combine with NH_3 to form complex ions. *Question.* Will a difficultly soluble salt of calcium, as CaCO_2 or CaC_2O_4 , dissolve in NH_4OH solution to a greater extent than in water?

14. *Problems.* (1) Write equations for the main reactions in the following experiments:

(a) A few drops of NH_4OH solution are added to a solution containing Zn^{++} .

(b) Excess NH_4OH solution is added to a solution containing Zn^{++} .

(c) An ammoniacal solution of silver chloride is acidified with nitric acid.

(2) The solubilities of AgCl and AgI in water are 10^{-4} and 10^{-7} mols per liter, respectively. In two experiments with NH_4OH solution each substance is found to be one thousand times more soluble than in water. How many grams of each has dissolved in 1 liter of the NH_4OH solutions?

(3) Give two examples of complex ions other than those with ammonia.

(4) From the positions of Cu , Ag , and Zn in the Periodic System (Hildebrand page 257), state what other ions might be expected to form ammonia complexes. Check your answer by referring to Hildebrand, page 269.

ASSIGNMENT 37

CARBONATES AND SULFIDES OF COPPER, SILVER AND ZINC

References. Hildebrand, pages 199-201 and 195-197.

1. In Assignment 33 we learned that when carbon dioxide dissolves in water the solution contains the weak acid H_2CO_3 , and in the saturated solution we recognized an equilibrium between H_2CO_3 in the solution and CO_2 in the gas space. We found that carbonic acid ionizes in two steps and can be neutralized in stages to give solutions of the two corresponding types of salts, and that when these salts are treated with a strong acid carbon dioxide is evolved. In the present Assignment we shall continue the study of difficultly soluble carbonates, and we shall deal with the salts of another dibasic acid, H_2S , which is in many respects analogous to carbonic acid.

2. Hydrogen sulfide, like carbon dioxide, is a gas which is soluble in water, and when the solution is saturated an equilibrium is established between gaseous and dissolved H_2S . The solution has the properties of a weak acid which ionizes in two stages as does carbonic acid. Sulfides, in general, are less soluble than carbonates; in the case of the alkali metals both the sulfides and carbonates are readily soluble, while in the case of the alkali earth metals the sulfides are readily soluble and the carbonates are not. *Questions.* Write the two equations which show the ionization of H_2S (dissolved in water) in two stages. What are the names of the negative ions formed? In analogy with the ions of carbonic acid, which is the stronger acid, H_2S or HS^- ? What are the principal substances present in a solution of sodium sulfide, Na_2S ? In a solution of sodium hydrogen sulfide, NaHS ? What reactions take place when a strong acid is added to any solution containing sulfide ion? How, then, will the solubility of difficultly soluble sulfides be affected by the addition of a strong acid?

3. *Experiment.* Try the action of Na_2CO_3 solution on 0.1 *N* solutions of Cu^{++} , Ag^+ , and Zn^{++} . In each case collect the precipitate on a filter, wash it with water, and test a portion for carbonate. Predict the action of nitric acid solution and of ammonium hydroxide on these precipitates, and test your prediction by experiments.

4. In the above experiment with Cu^{++} and in many other cases, the precipitate obtained by the addition of Na_2CO_3 to a solution of a salt is not a pure carbonate, but a substance which contains both the carbonate and hydroxide radicals. Such substances, called *basic carbonates*, are difficult to obtain pure, the actual precipitates consisting of variable mixtures of these basic carbonates, carbonates, and hydroxides.

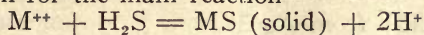
5. *Experiment.* Prepare 20 cc. of 0.1 *N* solutions of Cu^{++} , Ag^+ , and Zn^{++} . To each add 1 cc. 6 *N* H_2SO_4 and pass in H_2S gas* until the liquid is saturated. To determine this, close the end of the test-tube or flask, shake thoroughly and test the odor cautiously. Collect the precipitates on separate filters. In the experiment with Zn^{++} and H_2S , to the filtrate (or to the clear solution if there was no precipitate), add 10 cc normal NaAc solution, and again saturate with H_2S gas. *Question.* What effect has the addition of Ac^- on the concentration of H^+ ?

6. H_2S and HS^- are weaker acids than H_2CO_3 and HCO_3^- , respectively. What can you conclude about the relative concentrations of S^{--} and CO_3^{--} in solutions of H_2S and H_2CO_3 ? It will be recalled that H_2CO_3 does not precipitate CaCO_3

* Caution. H_2S is poisonous. Work out of doors if possible and do not breathe the gas.

from a solution of CaCl_2 (Assignment 33, Paragraph 6). *Question.* What conclusion can you draw with regard to the relative solubility of CaCO_3 and the sulfides prepared in the preceding Paragraph?

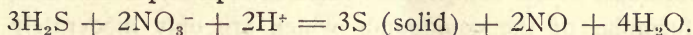
7. From the equation for the main reaction



it is evident that both M^{++} and H^+ are competing for S^{--} and that an increase in the H^+ concentration tends to reverse the reaction, as we have seen in the case of ZnS . However in the case of a very insoluble sulfide, CuS for example, even though H^+ concentration is fairly large the concentration of M^{++} will be negligible if the solution is saturated with H_2S . Determine by *experiment* which of these sulfides will dissolve completely in 2 N H_2SO_4 . Which then has the greater solubility in water? Write the two equations which show the mechanism of the main reaction. State how you would precipitate a sulfide which is sparingly soluble in water, but many times more soluble than ZnS (cf. the precipitation of CaCO_3).

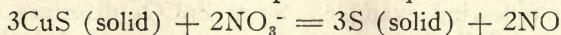
8. *Experiment.* To solutions containing $\text{Cu}(\text{NH}_3)_4^{++}$, $\text{Ag}(\text{NH}_3)_2^+$, and $\text{Zn}(\text{NH}_3)_4^{++}$, in separate experiments, add $(\text{NH}_4)_2\text{S}$ solution. Repeat the experiments, using H_2S gas instead of $(\text{NH}_4)_2\text{S}$ solution. State in each case which has the smaller concentration of the ion of the metal, a solution containing the complex ion, or a solution saturated with the sulfide. State also which is the less soluble in water, $\text{Cu}(\text{OH})_2$ or CuS , Ag_2O or Ag_2S , $\text{Zn}(\text{OH})_2$ or ZnS . From the fact that the sulfides are less soluble than the carbonates, predict the action of H_2S on mixtures of basic copper carbonate and water, silver carbonate and water, and zinc carbonate and water. Test your answers by *experiment*.

9. *Experiment.* Test the action of H_2S on solutions of nitric acid of different concentrations, 0.1 N, 2.0 N, and 6 N. Saturate each solution with H_2S gas and heat the mixture almost to boiling. The white precipitate formed is solid sulfur and the principal reaction is



Questions. What evidence is furnished by your experiments that this is a slow reaction? How is the speed affected by the concentration of the nitric acid, and by the temperature? (*Note.* The products of the reaction, S, NO, and H_2O , do not react with each other under any ordinary conditions of temperature and pressure, and it is practically impossible to realize an equilibrium involving the substances shown in the equation.) Because of this reaction nitric acid in a strongly acid solution will remove sulfide ion from the solution more completely than will H^+ alone since it destroys the H_2S which is in equilibrium with sulfide ion. We may therefore expect that nitric acid will be a better solvent for difficulty soluble sulfides than sulfuric or hydrochloric acid.

10. *Experiment.* Collect some CuS on a filter, transfer it to a casserole, add 2 normal HNO_3 and boil the mixture. Filter, and test the filtrate for Cu^{++} . The residue collected on the filter is sulfur; the dark color is due to a little CuS enclosed in the sulfur. Complete the equation



Problems. (1) Hydrogen sulfide is passed into 1 N CuSO_4 until the precipitation of copper sulfide is complete. The liquid is filtered and H_2S is removed by boiling. What concentration of H^+ is left in the solution.

(2) Write the equations for the neutralization of (a) one mol H_2S with one mol OH^- , (b) H_2S with excess OH^- , (c) HS^- with OH^- .

(3) Predict the effect of NH_4OH on the solubilities of CuS , ZnS and

Ag_2S . Give your reasoning. (If you try the experiments use freshly prepared sulfides moistened with water which contains H_2S .)

(4) Give a method for the preparation of

(a) CuSO_4 solution from CuS .

(b) Ag_2S (solid) from AgCl .

(c) ZnCO_3 (solid) from ZnS .

(d) Na_2CO_3 solution from Na_2S solution; see experiment at end of Paragraph 8, and Hildebrand, pages 207-208.

ASSIGNMENT 38

REVIEW OF THE CHEMISTRY OF THE POSITIVE IONS ALREADY CONSIDERED

1. This Assignment is inserted in order that the student may summarize and study the chemistry of the positive ions considered in the last seven Assignments. If the student makes an accurate summary, and notes carefully similarities and differences in the results for the various ions, he will find that it is not difficult to remember the large number of facts involved. In later work, as soon as the chemistry of another ion has been investigated, the results should be summarized, and compared with the results for the ions already studied.

2. *Summary of results.* Tabulate according to the following plan the results which you have obtained in earlier Assignments; refer to your laboratory notes whenever necessary. Write in a horizontal line across a double page of your notebook the names of the positive ions, silver, cupric copper, zinc, calcium, sodium, potassium and ammonium; in the vertical columns write the following:

(1) the formulas of the ions, including complex ions;

(2) the formulas of the compounds which are readily soluble in water.

(3) the formulas of the compounds which are only moderately soluble, as $\text{Ca}(\text{OH})_2$, CaSO_4 , Ag_2SO_4 .

(4) the formulas of the *insoluble* substances (the term difficultly soluble or sparingly soluble is preferable). Indicate which is the least soluble compound of each metal. When any ion or difficultly soluble compound is colored, give the color in the table. Next make as general statements as you can about the solubilities in water of the nitrates, chlorides, sulfates, carbonates, hydroxides (or oxides), and sulfides of these and other metals.

3. Show how you can apply your knowledge of the equilibria involved, in choosing reagents to dissolve the various difficultly soluble substances listed in the preceding Paragraph. In this connection, for each complex ion compare the concentration of the ion of the metal in a solution which contains the complex ion with that in a saturated solution of the various difficultly soluble salts of the metal; cf. Hildebrand's discussion of the reactions of silver ion, pages 204-205, and the following example. Since ZnCO_3 dissolves readily in excess NH_4OH solution, and ZnS does not, it may be concluded that in a solution which contains $\text{Zn}(\text{NH}_3)_4^{++}$ and NH_4OH the concentration of Zn^{++} is less than in a saturated solution of ZnCO_3 but greater than in a saturated solution of ZnS .

4. The Summary in Paragraph 2 was obtained from the results of experiments on the reactions between the positive ions and various reagents. Conversely the results of such experiments can be predicted by means of the Summary and a knowledge of the various equilibria involved.

5. *Table of Reactions.* Prepare for future reference a table of the reactions between dilute solutions of the positive ions considered above and the following reagents:

- (a) HCl or a soluble chloride,
- (b) NaOH in small amount,
- (c) NaOH in excess,
- (d) NH_4OH in small amount,
- (e) NH_4OH in excess,
- (f) H_2CO_3 or CO_2 gas,
- (g) a soluble carbonate,
- (h) H_2S in 0.3 N H^+ solution,
- (i) a soluble sulfide as Na_2S , or $(\text{NH}_4)_2\text{S}$ in NH_4OH solution,
- (j) sodium cobaltinitrite in the presence of a few drops of HAc.

When no reaction takes place mark X at the proper place in the table. In other cases write the formulas of the substances formed, note the colors, and mark the precipitates by underlining the formulas. Be sure that you can write the equation for each reaction. Try *experiments* whenever it is necessary, e. g. when your laboratory notes are incomplete or seem to be incorrect, and when there is a blank space in your table.

6. Test your knowledge of the reactions just considered by writing out from memory portions of the Table of Reactions, Paragraph 5; write equations for the reactions that take place, and discuss briefly the equilibria involved.

Note. It is recommended that the student proceed with Assignment 51, the first in the Section entitled Systematic Qualitative Analysis. It is important that the student become thoroughly familiar with the reactions already considered before proceeding to study other reactions, and this Assignment deals only with the ions already considered.

SECTION IV

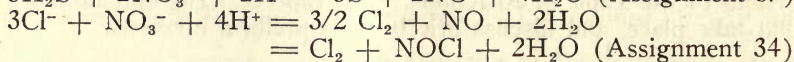
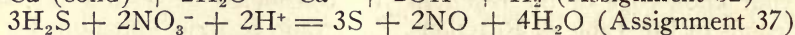
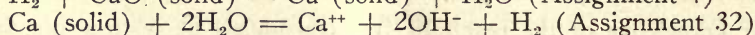
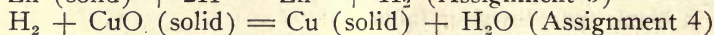
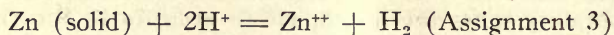
REACTIONS OF IONS, CONTINUED

ASSIGNMENT 41

OXIDATION AND REDUCTION. REPLACEMENT REACTIONS. ELECTRICAL CELLS

References. Hildebrand, Chapter VI pages 93-94, Chapter V page 70, Chapter XV pages 234-237.

1. In Assignment 41 and the three following Assignments we shall consider examples of *oxidation and reduction* reactions. In these reactions changes of valence occur, and they are therefore easily distinguished from other reactions such as the formation of weak electrolytes or the precipitation of difficultly soluble salts. The following reactions can now be recognized as oxidation and reduction reactions:



Point out the changes of valence in each reaction.

2. In the first of the above reactions the oxidation of Zn to Zn^{++} and the reduction of 2H^+ to H_2 consist simply in the transfer of two electrical charges from two hydrogen atoms to one zinc atom (which in reality is the transfer of two electrons from the zinc atom to the two hydrogen atoms). In the present Assignment we shall study a number of examples which are characterized by such an interchange of electrical charges. The reaction between copper and silver ion will first be studied quantitatively and then a number of other cases will be taken up qualitatively.

3. *Experiment.* Obtain at the office 100 cc. 0.10 *N* silver nitrate, and a special filter paper which burns to give an ash of negligible weight. Clean a straight piece of thin copper wire and weight about 0.3 g. to 5 mg. Cover the copper wire with 100 cc. of 0.10 *N* silver nitrate solution and let it stand until the copper has disappeared. The precipitate formed is metallic silver. *Questions.* What substance is responsible for the color of the final solution? What is the color of silver ion? Heat a porcelain crucible, let it cool, and weight to 5 mg. Collect the silver by filtering through the special filter paper and wash the precipitate until the washings are colorless. (Save the filtrate, and place in it another piece of copper in order to recover the rest of the silver.) Fold the filter paper so that it will fit into the crucible, heat with a small flame until it is dry, and then with a larger flame until the paper is completely consumed. Let the crucible cool and again weigh to 5 mg. Place all the silver in the jar marked "Silver Waste."

4. *Calculations.* Calculate (a) the weight of silver formed in the experiment; (b) the weight of silver precipitated by one gram atom of copper. Compare the latter number with the atomic weight of silver. (The formula of silver ion is Ag^+ .) What is the formula of copper ion?

5. *Questions.* Give the formulas of silver nitrate, silver sulfate, copper nitrate and copper sulfate. If one gram molecule of silver ion has associated with it 96,500 coulombs of positive electricity what quantity of electricity is

associated with one gram molecule of copper ion? With a gram molecule of nitrate ion? Write the equation for the action of silver ion on copper. How would the result of this experiment have been influenced by replacing the silver nitrate with silver sulfate solution?

6. *Experiment.* Into 10 cc. $N\text{ Cu}(\text{NO}_3)_2$ place a piece of lead.

7. Repeat the *experiment* with a solution of lead nitrate, $\text{Pb}(\text{NO}_3)_2$, and zinc.

8. Write the equations for all the reactions between metals and positive ions which you have studied (Assignments 3 and 41). *Questions.* The negative ion present in each experiment is not shown in the equation; what experimental fact is thereby implied? If in one of the above experiments the dry salt had been used instead of its solution, would the reaction occur sufficiently rapidly at room temperature to be detected? Try an *experiment*, if necessary, with lead and solid copper sulfate.

9. *Experiment.* Determine by experiment which of the metals used in this Assignment will dissolve readily in dilute hydrochloric acid (or sulfuric acid).*

10. Arrange the metals used in these experiments in the order in which they will replace each other from solution. After referring to your lecture notes state where hydrogen belongs in this *replacement series*. From this replacement series predict what will happen when,

Silver nitrate solution is treated with lead.

Copper nitrate " " " " zinc.

Copper nitrate " " " " silver.

Experiment. Test the correctness of your prediction.

11. *Replacement series for the halogens.* *Experiment.* Make a small gas generator (see Assignment 33, Paragraph 3) and charge the flask with about 2 g. of manganese dioxide. Pour 5 cc. concentrated HCl into the flask and warm gently until a continuous stream of chlorine is evolved. Pass a few bubbles of the gas through a very dilute solution of potassium bromide, prepared by diluting a few drops of the laboratory solution with 5 cc. water. Shake the solution with 1 cc. of carbon bisulfide. The brown color in the carbon bisulfide layer is characteristic of bromine.

12. *Experiment.* To 1 cc. potassium iodide solution add a drop of bromine water. Shake with carbon bisulfide. The violet color is characteristic of iodine.

13. *Questions.* In each of the above experiments write the equation for the reaction which has taken place. Point out the changes of valence and the interchange of electrical charges. Predict what reaction will occur when (a) chlorine gas is passed through KI solution, (b) bromine is added to KCl solution, and (c) iodine is added to KBr solution. *Experiment.* Test the correctness of your predictions.

14. *The Conversion of Chemical into Electrical Energy.* The reactions studied in the present Assignment may be utilized to convert chemical into electrical energy. In each of the reactions an interchange of electrical charges has taken place; and the problem in the construction of an electrical cell is to arrange the substances involved in the reaction in such a way that this interchange of electricity can take place only through an external conductor such as a wire joining the electrodes. Thus, in the reaction between zinc and copper ion two changes of an electrical nature are involved: on the one hand zinc is changed to zinc ion, and, on the other, copper ion is changed to copper. When the zinc

*The action of nitric acid on metals will be studied in Assignment 42.

is placed directly in a solution of a copper salt the electrical changes both occur at the surface of the zinc and the transfer of electricity cannot be directly detected; but when we arrange the materials so that the zinc electrode dips into a zinc sulfate solution contained in a porous cup, and this is placed in a vessel containing copper sulfate solution and the copper electrode, then no reaction takes place. If now we join the two electrodes by a wire, electricity passes through the wire and zinc will change to zinc ion at the surface of the zinc, while copper ion changes to copper at the surface of the copper. The total change in the cell is of course the same as when zinc acts directly on copper ion.

15. Draw a diagram of the electrical cell described above. *Question.* What substances carry the electricity from one electrode to the other through the solution?

16. In a similar way the reaction between chlorine and bromide ion may be used to generate electrical energy; but, to lead the current into and out of the solution, we must use some substance, as graphite, which conducts electricity and is not attacked by chlorine or bromine. In one part of this electrical cell there would thus be a graphite rod dipping into a solution which contains bromide ion and bromine, and in the other part a graphite rod in a solution of chloride ion and chlorine. The two solutions must be separated, e. g., by a porous cup, in order to prevent the chlorine from reacting directly with the bromide ion. When the graphite electrodes are joined by a wire a current will flow, and at the one electrode bromide ion will change to bromine while at the other electrode chlorine will change to chloride ion.

17. *Problems.* (1) What quantity of electricity (in coulombs) flows through the circuit of the cell described in Paragraph 13 when one mol of zinc disappears? What weight of copper will at the same time be deposited on the copper electrode?

(2) Sketch the arrangement of a cell in which the reaction between metallic copper and silver ion is used to produce an electric current. When a current is taken from this cell what changes take place at each electrode?

(3) How many coulombs of electricity could be obtained by the transformation of 1 liter chlorine gas (measured at 0° C and 760 mm.) to chloride ion?

ASSIGNMENT 42

OXIDATION OF METALS TO THEIR IONS. TABLE OF OXIDIZING AND REDUCING AGENTS

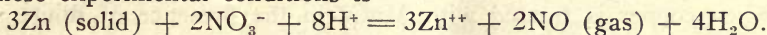
Reference. Hildebrand, Chapter XV pages 226-245.

1. In Assignment 41 we found that certain metals can be oxidized by hydrogen ion and that other metals cannot. We may say, therefore, that certain metals are sufficiently strong reducing agents to reduce hydrogen ion to hydrogen and that others are not, and it follows that any reagent which will change one of the latter metals to its ion is a more powerful oxidizing agent than is hydrogen ion. In the present Assignment we shall study the action on zinc, copper, and silver of two such oxidizing agents, nitric acid and bromine.

2. Arrange copper, silver, zinc and hydrogen, in a vertical column, in a replacement series. Beside each symbol write the formula of the ion to which the element can be oxidized. Your table now is a *table of oxidizing and reducing agents* arranged according to their strengths, and this table

may be extended to include other substances than the metals and their ions. *Questions.* Which is the more powerful reducing agent, Zn or Cu? Cu or Ag? Which is the more powerful oxidizing agent, Ag^+ or Cu^{++} ? Ag^+ or H^+ ? (State the experimental facts upon which you based your answers to the preceding questions.) In describing the reaction between zinc and dilute hydrochloric or sulfuric acid solution is it correct to say that metallic zinc has combined with chloride ion or with sulfate ion? How can the solid salts be prepared from the solutions obtained in such experiments?

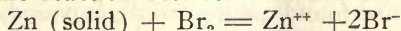
3. *Action of nitric acid on zinc, copper, and silver. Experiment.* Treat about $\frac{1}{4}$ grams of zinc with 2 N HNO_3 in a small beaker, covered with a watch-glass. If the reaction is slow warm the mixture. The main reaction under these experimental conditions is



4. Repeat the *experiment* with about 0.5 g. copper, and with a small piece of silver. The reactions are similar to the one between zinc and nitric acid, and the change from Zn to Zn^{++} corresponds exactly to the change from Cu to Cu^{++} and from 2 Ag to 2 Ag^+ . Write the equations for the reactions. *Question.* How is the speed of the reaction between nitric acid and the metals affected by a change in temperature and by a change in the concentration of the acid?

5. *Action of bromine on zinc, copper and silver.* The halogens, chlorine, bromine and iodine, all have a similar action on metals. To illustrate this action we use bromine because its aqueous solution is a convenient reagent. The solution of chlorine in water does not keep well, while iodine is a solid which is only very slightly soluble in water. *Experiment.* Treat a small piece of zinc with bromine water. After a few minutes pour the solution into a porcelain dish, and heat it to boiling to expel any bromine that is present. To a portion of the solution add a few drops of silver nitrate: AgBr , like AgCl and AgI , is a difficultly soluble salt. Test another portion of the solution for zinc ion. What evidence have you that a reaction takes place between zinc and bromine? Repeat the *experiment* with copper and bromine water. Silver, also, reacts with bromine.

6. The equation for the reaction between zinc and bromine solution is



Since in this reaction zinc is oxidized to zinc ion we must conclude that bromine is reduced when it changes to bromide ion. Write the equation for the action of bromine on copper and on silver.

7. Review the replacement series for the halogens (Assignment 41) and arrange chloride ion—chlorine, bromide ion—bromine, iodide ion—iodine in a table so as to give the relative strengths of the halogens as oxidizing agents and of the halide ions as reducing agents. Add this table, in its proper place, to the one previously prepared for the metals and their ions. Place $\text{Ca} - \text{Ca}^{++}$ and $\text{Na} - \text{Na}^+$ in this table. Show your completed table at once to the instructor.

8. We can determine the position of nitric acid in this table of oxidizing and reducing agents by reference to the results of the experiment in Paragraph 6, Assignment 34, when hot concentrated nitric acid was used to remove chloride ion from a solution. Chlorine was formed and we can therefore decide that hot concentrated nitric acid is a stronger oxidizing agent than chlorine. *Question.* Is concentrated nitric acid a stronger oxidizing agent than bromine or iodine?

9. Study the method of balancing oxidizing and reducing reactions. Hildebrand, pages 226-233.

10. *Problems.* (1) Summarize the behavior of Na, K, Ca, Zn, Cu, and other

metals discussed in the lectures by dividing the metals into the three following classes:

- I. Those which react readily with water. Hydrogen is evolved.
- II. Those which react readily with HCl or H_2SO_4 solution, but not with water. Hydrogen is evolved.
- III. Those which dissolve readily in HNO_3 or Br_2 solution, but not in HCl, H_2SO_4 or water. H_2 is not evolved.

Write the equation for the action of HCl or H_2SO_4 solution on metallic sodium.

(2) In the experiment in Paragraph 11, Assignment 41, manganese dioxide, MnO_2 , reacted with chloride ion in acid solution to form chlorine. Manganous ion, Mn^{++} , was formed. Write the equation for the reaction. Predict what will happen when copper is treated with MnO_2 in the presence of dilute sulfuric acid.

(3) Sketch the arrangement of a cell in which the reaction between zinc and bromine is used to produce an electric current. What changes take place at the electrodes? State how you could bring about the reversal of all the reactions in this cell.

ASSIGNMENT 43

FERROUS AND FERRIC IONS

Reference, in this and later Assignments: A standard text on Inorganic Chemistry. *Note*. Read again Assignment 31, Paragraph 2, and Assignment 38.

1. In Assignment 43 we shall study the chemistry of iron as an example of a metal which forms two series of compounds in which the valence of the metal is different. You will find on the laboratory shelves solutions and solid salts of ferrous and of ferric iron. Give the valences of the following: sulfate ion; sulfate in ferrous sulfate, FeSO_4 ; Fe (metal); ferrous ion, Fe^{++} ; ferric ion, Fe^{+++} ; iron in a ferrous salt, and in a ferric salt. Write the formulas of the chlorides, nitrates, hydroxides, and oxides of ferrous and of ferric iron.

2. Many *double salts* are found among iron compounds.

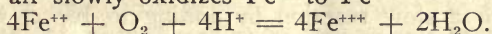
$\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, ferrous ammonium sulfate, and

$\text{Fe}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$, ferric ammonium sulfate (ammonium iron alum) are examples of double salts whose solutions dissociate into the ions of the simple salts. These two salts may be used in studying the properties of Fe^{++} and Fe^{+++} , respectively. Give the formulas of: *alum*, potassium iron alum, sodium iron alum.

3. The ferrocyanides and ferricyanides are examples of double salts whose solutions contain complex ions at high concentrations. The formula, $\text{Fe}(\text{CN})_2 \cdot 4\text{NaCN}$, for sodium ferrocyanide shows its relation to the simple salts. It can be prepared by dissolving the difficultly soluble ferrous cyanide, $\text{Fe}(\text{CN})_2$, in excess of NaCN, but in a solution of the pure salt the concentrations of Fe^{++} and CN^- are extremely small. Accordingly the formula is usually written $\text{Na}_4\text{Fe}(\text{CN})_6$ to show that the ferrocyanide radical $\text{Fe}(\text{CN})_6$ is the negative constituent of the salt. Similarly $\text{Na}_3\text{Fe}(\text{CN})_6$ is the formula usually written for sodium ferricyanide. *Questions*. What is the valence of the ferrocyanide radical? Of the ferricyanide radical? What is the formula of potassium silver cyanide? How is it prepared? What ions are present in its solution? *Caution*. Soluble cyanides and hydrocyanic acid are deadly poisons: do not try unnecessary experiments with them. Ferro and ferricyanides are not dangerous.

4. *Color tests for Fe⁺⁺ and Fe⁺⁺⁺. Experiment.* To a dilute solution of FeCl₃ add a drop or two of K₄Fe(CN)₆ solution. Repeat with K₃Fe(CN)₆. Prepare a solution of a ferrous salt by dissolving a small amount of FeSO₄ or of FeSO₄ · (NH₄)₂SO₄ in a little dilute sulfuric acid, and test portions of this solution at once with K₄Fe(CN)₆ and with K₃Fe(CN)₆. The characteristic dark blue precipitates, or colloidal solutions, obtained in two of these four experiments are probably identical. Equations may be omitted for these reactions.

5. *Oxidation of Fe⁺⁺ to Fe⁺⁺⁺. Experiment.* Test for Fe⁺⁺⁺ an acid solution of FeSO₄ which has been standing in the laboratory for several days. The oxygen of the air slowly oxidizes Fe⁺⁺ to Fe⁺⁺⁺



Experiment. To a few drops of a ferrous salt solution in a porcelain dish add a little HNO₃, heat the mixture, dilute with water, and test whether the solution now contains Fe⁺⁺ or Fe⁺⁺⁺. Try an *experiment* with another oxidizing agent and determine whether or not it oxidizes Fe⁺⁺ to Fe⁺⁺⁺.

6. *Note. Write equations for all reactions.*

7. *Reaction between Fe and Fe⁺⁺⁺. Experiment.* Place some iron wire or iron filings in a very dilute solution of FeCl₃, stir the mixture, and test small portions of the solution from time to time for Fe⁺⁺ and Fe⁺⁺⁺.

8. *Reactions of iron with H⁺, and with Cu⁺⁺. Experiment.* Try the action of dilute HCl or H₂SO₄ on a small piece of iron; heat the mixture, if necessary. Predict whether ferrous or ferric ion is formed, and test the correctness of your answer. *Experiment.* Cover a small piece of iron with a solution of a copper salt.

9. From the results of the above experiments, or from any other source of information, determine approximately the position of Fe—Fe⁺⁺ and of Fe⁺⁺—Fe⁺⁺⁺ in your table of oxidizing and reducing agents, Assignment 42, Paragraphs 2 and 7. It is not advisable to attempt to assign a definite place in one large table to each of the oxidizing and reducing agents which you will study. Thus in the case of Fe⁺⁺—Fe⁺⁺⁺ it is sufficient to note that Fe⁺⁺—Fe⁺⁺⁺, I—I₂ and Ag—Ag⁺ are in the same part of the table: Fe⁺⁺, I⁻ and metallic silver are all readily oxidized by powerful oxidizing agents, while Fe⁺⁺⁺, I₂ and Ag⁺ are easily reduced by powerful reducing agents. *Questions.* Which is the stronger reducing agent, Fe⁺⁺ or Fe? Which is the stronger oxidizing agent, Fe⁺⁺⁺ or Fe⁺⁺?

10. *Reduction of Fe⁺⁺⁺ by H₂S in acid solution. Experiment.* To a few drops of FeCl₃ solution add 1 cc. 6 N HCl and about 20 cc. water, and saturate the solution with H₂S gas. Boil the mixture in a porcelain dish to coagulate the precipitated sulfur and expel the H₂S, filter and at once test a portion of the clear solution for Fe⁺⁺⁺. Treat the remainder of the solution again with H₂S if Fe⁺⁺⁺ seems to be present. Name another reducing agent which might be expected to reduce Fe⁺⁺⁺ to Fe⁺⁺ and try the *experiment*.

11. *Other reactions of Fe⁺⁺⁺. Experiments.* Treat small quantities of dilute solutions of FeCl₃ with the following reagents:

- NH₄OH in small amount and in excess. The precipitate is Fe(OH)₃.
- NaOH in small amount and in excess.
- Na₂CO₃ or (NH₄)₂CO₃. Filter; acidify the filtrate and test it for Fe⁺⁺⁺ with K₄Fe(CN)₆; wash with water the precipitate (obtained by adding carbonate), and test whether it is a carbonate or hydroxide.
- NH₄OH or NaOH and then a sulfide as H₂S or (NH₄)₂S. The black precipitate is mainly Fe₂S₃, but may contain some FeS and S.

12. *Other reactions of Fe^{++} .* Repeat the *experiments* in (11) with small quantities of dilute solutions of ferrous salt. In (a) and (b) note what happens when moist ferrous hydroxide is exposed to the air; the oxygen reacts much more rapidly with moist $Fe(OH)_2$ than with Fe^{++} in acid solution. The brown compound formed in the test for nitrate ion, Assignment 31, Paragraph 13, is an addition compound of NO and ferrous ion, probably $Fe(NO)^{++}$. This compound is formed when NO gas is passed into a cold ferrous salt solution, and when nitric acid, nitrous acid, or NO_2 is reduced by excess Fe^{++} . *Questions.* What happens when a solution which contains this addition compound is heated? Is the rate of reduction of nitrate ion in dilute acid solution by Fe^{++} a rapid or a slow reaction? *Experiment.* Determine whether the reduction of nitrous acid, HNO_2 , is a rapid or a slow reaction by adding to 10 cc. water, 2 cc. $FeSO_4$ solution, a few drops of 6 N H_2SO_4 , and a drop of a nitrite solution.

13. Summarize in a table for future reference the reactions of Fe^{++} and Fe^{+++} with the following reagents: a strong oxidizing agent, as hot moderately concentrated HNO_3 ; a strong reducing agent, as zinc in acid solution; H_2S in 0.3 N acid solution, and the reagents used in Paragraphs 11 and 12. Below the table give methods of dissolving the difficultly soluble salts of iron which you have studied.

14. *Problems.* Try experiments when necessary.

(1) How would you transform

- (a) ferric chloride to ferric sulfate;
- (b) ferric sulfate to ferric chloride;
- (c) ferrous sulfate to ferric sulfate;
- (d) ferric sulfate to ferrous sulfate?

(2) $Fe(OH)_2$ is moderately soluble in a solution of an ammonium salt, as NH_4Cl , and $Fe(OH)_3$ is not. Outline an experiment to demonstrate this. Which is the less soluble in water, $Fe(OH)_2$ or $Fe(OH)_3$?

(3) Suggest a method of preparing $Fe(OH)_3$ and ZnS from a single portion of a solution which contains Fe^{++} , Zn^{++} , H^+ and SO_4^{--} .

ASSIGNMENT 44

MERCUROUS AND MERCURIC IONS

1. In the present Assignment we shall study the chemistry of another metal which forms two series of compounds. You will find on the laboratory shelves solutions of mercurous nitrate, $HgNO_3$; and of mercuric nitrate, $Hg(NO_3)_2$. What is the valence of mercury in a mercurous salt; in a mercuric salt? Write the formulas of the chlorides, sulfates and oxides of mercurous and of mercuric mercury.

2. *Mercurous chloride and mercuric chloride. Experiment.* To 1 cc. N $HgNO_3$ add 20 cc. water and 1 cc. 6 N HCl. Repeat the experiment with N $Hg(NO_3)_2$, and give a method of distinguishing between soluble mercurous and mercuric salts. *Note.* Mercuric chloride is one of the few examples of a *weak salt*. The concentrations of Hg^{++} and of Cl^- in its solution are very small.

3. *Reduction of mercuric ion in stages.* Tin forms two series of compounds stannous and stannic, in which the valence of tin is + 2 and + 4 respectively. Stannous ion, Sn^{++} , is a good reducing agent since it is easily oxidized to Sn^{+++} . The chlorides of tin are both soluble in water; and the common stannous salt laboratory reagent is $SnCl_2$ solution to which HCl has been added to prevent

the precipitation of a basic salt. *Experiment.* To 1 cc. $N \text{ Hg}(\text{NO}_3)_2$ and 20 cc. water add one drop SnCl_2 solution. Divide the mixture into two portions and to one portion add SnCl_2 until it is present in excess. Observe the difference in appearance of finely divided mercury and a large drop of the metal. Suggest a method of testing a solution for the presence of mercuric mercury. Try your method with a dilute solution of HgCl_2 .

4. *Reaction between mercuric ion and mercury. Experiment.* To 1 cc. $N \text{ Hg}(\text{NO}_3)_2$ add a drop of mercury, shake the mixture gently, and after several minutes add 20 cc. water. Pour off the solution and test it for Hg^+ with HCl . Filter off the mercurous chloride and test the filtrate for mercuric mercury. If there is more than a mere trace repeat the experiment and leave the mercury in contact with the solution for a long time. The reaction between Hg and Hg^{++} is similar to that between Fe and Fe^{+++} . In each case, in the presence of excess of the metal, the reaction will proceed until at equilibrium the concentration of the ion of higher valence, Hg^{++} or Fe^{+++} , is extremely small. *Questions.* Which is the stronger oxidizing agent, Hg^{++} or Hg^+ ? Which is the stronger reducing agent, Hg^+ or Hg ?

5. *Reduction of Hg^+ and oxidation of Hg .* By experiments with some of the metals you have studied and small amounts of HgNO_3 solution determine approximately the position of $\text{Hg} - \text{Hg}^+$ in your table of oxidizing and reducing agents. In these experiments any metallic mercury formed can usually be seen on the surface of the metal, but the solution may also be tested for the dissolved metal after precipitating the mercurous mercury with HCl . From your result predict whether metallic mercury will dissolve in dilute sulfuric acid, and test your prediction. *Experiment.* Treat a very small drop of mercury with about 30 cc. $2 N \text{ HNO}_3$ in a porcelain dish or beaker. If the reaction is slow heat the mixture. While the reaction is in progress pour a small amount of the solution into 10 cc. water and test for Hg^+ and Hg^{++} . When a moderate amount of the metal has dissolved, pour off the solution for use in the next experiment.

6. *Oxidation of Hg^+ and of HgCl .* *Experiment.* Continue the preceding experiment to determine how rapidly hot $2 N \text{ HNO}_3$ oxidizes Hg^+ . Repeat the experiment with hot concentrated HNO_3 and a small quantity of HgNO_3 . *Experiment.* Collect some HgCl on a filter. Treat a small portion in a porcelain dish with hot $2 N \text{ HNO}_3$, and another portion with hot $2 N \text{ HNO}_3$, to which some HCl has been added. Repeat the experiments, if necessary, with more concentrated HNO_3 , and note whether the speed of oxidation is increased by the presence of HCl . *Experiment.* Treat a small portion of HgCl with bromine water, and test the solution as before for mercuric mercury.

7. *Difficulty soluble salts of mercuric mercury. Experiment.* Test the action of each of the following reagents on a dilute solution of $\text{Hg}(\text{NO}_3)_2$. Save the precipitate for use in (8).

(a) H_2SO_4 or a soluble sulfate.

(b) Na_2CO_3 . The precipitate is a basic carbonate.

(c) NaOH . The precipitate is HgO .

(d) NH_4OH . When a chloride is present the precipitate is $\text{Hg}(\text{NH}_2)\text{Cl}$, ammonobasic mercuric chloride, which is closely related to $\text{Hg}(\text{OH})\text{Cl}$, basic mercuric chloride. Analogous but more complex substances are precipitated in the absence of chloride. What is the valence of the OH radical? Of the NH_2 radical?

(e) H_2S in acid solution.

8. Predict the action of dilute HCl or HNO_3 on each of the precipitates just obtained (except HgS), and test your answers by experiments.

9. *Experiment.* Collect some HgS on a filter and wash it with water. Transfer part of the precipitate to a porcelain dish, add 2 N HNO_3 , boil the mixture for about a minute, and filter. Test the filtrate for Hg^{++} . Repeat the experiment with hot 2 N HNO_3 to which some HCl has been added. From the fact that HgCl_2 is a weak salt suggest an explanation for the result of this experiment. Repeat the *experiment* with bromine solution instead of HNO_3 .

10. *Other reactions of mercurous ion. Experiment.* Treat a dilute solution of HgNO_3 with each of the following reagents:

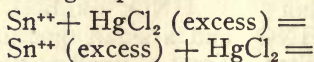
- (a) H_2SO_4 or a soluble sulfate.
- (b) Na_2CO_3 .
- (c) NaOH . The precipitate is Hg_2O , which, on heating, decomposes into Hg and HgO .
- (d) NH_4OH . The precipitate is a mixture of metallic mercury and an ammonobasic mercuric salt; see 7 (d).
- (e) H_2S in acid solution. The precipitate is a mixture of Hg and HgS .

11. From the results of your experiments in Paragraphs 6, 8, and 9, give methods of dissolving each of the precipitates obtained in 10. Try experiments whenever you are doubtful of your method.

12. *Table of reactions for mercurous ion and mercuric ion.* Summarize in a table for future reference the reactions of Hg^+ and Hg^{++} with the following reagents: HCl ; a strong oxidizing agent as Br_2 , a strong reducing agent as SnCl_2 (in small amount and in excess), and the reagents used in Paragraphs 7 and 10. Below this table classify the precipitates according to reagents used in dissolving them and point out the considerations that led to the choice of each reagent. Be sure that you can write the equation for each reaction.

13. *Problems.* Try experiments when necessary.

(1) Complete the following equations, and indicate what you would observe in the corresponding experiments:



(2) What reactions are possible between a sulfide and hydrochloric acid? Between a sulfide and nitric acid? In connection with your answers discuss the following experimental facts; CuS dissolves readily in hot 2 N HNO_3 but not in hot 2 N HCl .

(3) Compare the action of hot 2 N HNO_3 on CuS (Assignment 37 Paragraph 10) and HgS , and state what conclusion can be drawn with regard to the relative solubilities of these two sulfides in water. Outline a method of preparing pure HgCl_2 and pure CuSO_4 from a mixture of the freshly precipitated sulfides.

(4) Suggest methods of making the following preparations:

- (a) HgO from $\text{Hg}(\text{NO}_3)_2$;
- (b) $\text{Hg}(\text{NO}_3)_2$ from HgSO_4 ;
- (c) $\text{Hg}(\text{NO}_3)_2$ from HgNO_3 ;
- (d) HgNO_3 from $\text{Hg}(\text{NO}_3)_2$.

Note. It is recommended that Assignment 52 on Qualitative Analysis, follow Assignment 44.

ASSIGNMENT 45

LEAD ION, CHROMATE ION

1. In the present Assignment and the following ones we shall continue the study of important common elements. Only very brief laboratory directions will be given; each student is expected to plan the details of the experiments, and is recommended to try additional experiments which are suggested by the lectures or laboratory work.

2. *Chromate ion*, CrO_4^{--} , and *bichromate ion*, $\text{Cr}_2\text{O}_7^{--}$. Note the colors of solutions of sodium (or potassium) chromate and bichromate. What is the color of CrO_4^{--} ? Of $\text{Cr}_2\text{O}_7^{--}$? What is the valence of chromium in these ions? *Experiment*. Add dilute HNO_3 or H_2SO_4 to a small quantity of a chromate solution. Add dilute NaOH or NH_4OH to a bichromate solution; acidify the solution obtained. *Note*. Many chromates are difficultly soluble in water, but dissolve in HNO_3 .

3. *Reactions of lead ion*, Pb^{++} . *Experiment*. Treat small portions of 0.1 N $\text{Pb}(\text{NO}_3)_2$ with each of the reagents listed in Assignment 38 (Paragraph 5), with H_2SO_4 , and with a soluble chromate.

4. *Methods of dissolving difficultly soluble lead salts*. State which of the precipitates obtained in (3) you would expect to dissolve in 0.2 N HNO_3 . *Experiment*. Prepare some PbS , collect it on a filter, and test portions of it with hot 2 N HCl , and with hot 2 N HNO_3 . *Experiment*. Collect some PbCl_2 on a filter, pour cold water over it and test the filtrate for Pb^{++} , e. g. with H_2S ; then pour hot water over PbCl_2 on a filter and test the filtrate for Pb^{++} . *Experiment*. Collect some PbCrO_4 on a filter, wash thoroughly with water to remove any soluble chromate, and determine how readily it dissolves in hot dilute HNO_3 . What ions are present in the solutions obtained? *Experiment*. Collect some PbSO_4 on a filter, transfer some of it to a test tube, and pass in H_2S . Which is the less soluble, PbSO_4 or PbS ? *Experiment*. Treat some PbSO_4 with Na_2CO_3 solution, as directed in Assignment 52, 11 (5).

5. *Relative delicacy of tests for Pb^{++}* . *Experiment*. Prepare 50 or 100 cc. portions of 0.01 N, 0.001 N, 0.0001 N $\text{Pb}(\text{NO}_3)_2$. Test 5 or 10 cc. of each solution with the reagents used in (3). Specify the two most delicate tests. Name the two least soluble salts of lead.

6. *Lead dioxide*, PbO_2 . *Experiment*. Treat a small portion of PbO_2 with hot 6 N HCl . What gas is evolved? Repeat the experiment with HNO_3 instead of HCl .

7. *Problems*. (1) Outline methods for making the following transformations:

- | | |
|---------------------------------------|--|
| (a) PbSO_4 to PbS . | (c) PbCO_3 to PbCrO_4 . |
| (b) PbS to PbSO_4 . | (d) PbO_2 to $\text{Pb}(\text{NO}_3)_2$. |

(2) Name three amphoteric hydroxides, (cf. Assignment 35). What would be observed on gradually acidifying a solution of sodium plumbite?

ASSIGNMENT 46

STANNOUS AND STANNIC IONS. AMPHOTERIC SULFIDES

Reference. Hildebrand, pages 197-199.

1. *Ammonium polysulfide solution*. *Experiment*. Prepare some colorless ammonium sulfide solution by passing H_2S into NH_4OH solution. Divide the solution into three parts. To one portion add a very small amount of powdered

sulfur. Place another portion on a watch-glass to expose it to the action of the oxygen of the air. Acidify the third portion with dilute HCl. *Experiment.* Acidify small quantities of the laboratory solutions of ammonium polysulfide (yellow ammonium sulfide), and of ammonium sulfide. *Note.* On account of hydrolysis the $(\text{NH}_4)_2\text{S}$ solution is really $\text{NH}_4\text{OH} + \text{NH}_4\text{SH}$.

2. *Reactions of Sn^{++} and Sn^{++++} .* *Experiment.* Prepare 0.1 N solutions of stannous chloride and of stannic chloride, and determine the action of the following reagents on each of these solutions:

- (a) H_2S in cold 0.3 N HCl solution. These tests are delicate and characteristic.
- (b) H_2S in hot 2 N HCl. If there is a precipitate, filter, add water to the filtrate and test it for tin.
- (c) NH_4OH in small amount and in excess.
- (d) NaOH in small amount and in excess. If there is a precipitate after adding NaOH in excess, filter, acidify the filtrate with HCl or H_2SO_4 and test it for tin.
- (e) $(\text{NH}_4)_2\text{S}$ after NH_4OH has been added.
- (f) Ammonium polysulfide after NH_4OH has been added. Pour through a filter to remove any precipitate that may remain undissolved, and acidify with dilute HCl.
- (g) A soluble carbonate. Filter, wash the precipitate and test it for carbonate.
- (h) A good oxidizing agent in dilute acid solution, such as bromine.
- (i) A good reducing agent in dilute acid solution, as zinc.
- (j) HgCl_2 solution in small amount and in excess.

3. *Action of concentrated HNO_3 on Sn.* *Experiment.* Treat a small piece of tin with concentrated HNO_3 in a casserole. Evaporate the mixture *just to dryness*: to avoid heating the residue strongly, evaporate the last portions of the liquid by moving the casserole back and forth through a small flame. Warm the residue with dilute HNO_3 , filter, and test the filtrate for tin. *Note.* Stannic acid, or hydrated stannic oxide, when prepared in this way by the action of concentrated HNO_3 on Sn or on a compound of tin, is difficultly soluble in HNO_3 . *Experiment.* Suggest and try methods of dissolving this substance.

4. *Problems.* (1) If a solution were known to be either SnCl_2 or SnCl_4 how would you identify it?

(2) How would you test for SnCl_2 in a solution of SnCl_4 ?

(3) What happens when HCl is added gradually to a solution of (a) sodium stannite, (b) sodium stannate, (c) sodium stannite after it has been treated with a powerful oxidizing agent, as sodium peroxide, Na_2O_2 , or hypochlorite, (d) sodium sulfostannate?

(4) How would you prepare (a) ammonium polysulfide, (b) sodium sulfo-stannate from SnS_2 , (c) sodium sulfostannate from SnS ?

ASSIGNMENT 47

IONS OF ALUMINUM AND OF CHROMIUM. PEROXIDES

1. Write the formulas of aluminum chloride, nitrate and sulfate; chromium chloride, nitrate and sulfate; alum and chrom alum. These salts are all readily soluble in water and their solutions react acid to litmus.

2. *Hydroxides.* *Experiment.* To very dilute solutions of an aluminum salt and of a chromium salt add NH_4OH a few drops at a time until, after shaking, the odor of ammonia is just perceptible. Warm the mixture. These are delicate tests for Al^{+++} and Cr^{+++} .

3. When a solution of an aluminum, or chromium, salt is treated with a soluble carbonate or sulfide, the hydroxide of aluminum, or chromium, is precipitated. Explain.

4. *Aluminate ion and chromite ion.* AlO_2^- and CrO_2^- (or H_2AlO_3^- and H_2CrO_3^-). *Experiment.* To dilute solutions of an aluminum salt and of a chromium salt add a few drops of NaOH solution. To each mixture add more NaOH and shake after each addition. Filter if a precipitate remains, add some solid ammonium salt, and heat the mixture.

5. *Ions of Chromium.* State which ions of chromium can exist only in an acid solution and which in an alkaline solution. What is the valence of chromium in each of these ions? Suggest a method of changing bichromate ion to chromic ion.

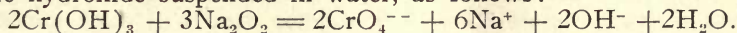
6. *Reduction of $\text{Cr}_2\text{O}_7^{--}$ and of CrO_4^{--} .* *Experiment.* Test the action of H_2S on very dilute solutions of a bichromate in the presence of sulfuric acid, heat the mixture to boiling, filter, and wash the precipitate. Make the filtrate alkaline with NH_4OH . Repeat the *experiment* with H_2S and a very dilute solution of a chromate in the presence of NaOH , heat, filter and wash the precipitate. Acidify the filtrate. *Experiment.* Determine the action of hot concentrated HCl on $\text{Cr}_2\text{O}_7^{--}$, and of Cl^- on CrO_4^{--} in alkaline solution.

7. *Oxidation of chromite ion.* *Experiment.* Prepare a small quantity of a chromite solution. To a portion of this add bromine solution; boil the solution to expel any bromine that may remain. *Question.* How would you prepare a hypochlorite solution? Write the equation for the oxidation of CrO_2^- by ClO^- . *Experiment.* Boil a small quantity of a chromic salt solution with concentrated HNO_3 , or with aqua regia.

8. *Peroxides.* Sodium peroxide decomposes rapidly, even in a cold solution.

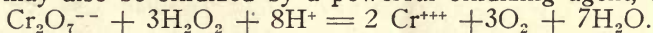
$$\text{Na}_2\text{O}_2 + \text{H}_2\text{O} = 2\text{NaOH} + \frac{1}{2}\text{O}_2$$

Hydrogen peroxide in a cold, dilute acid solution decomposes only very slowly. Na_2O_2 is a very powerful and useful oxidizing agent. It reacts with chromic hydroxide suspended in water, as follows:

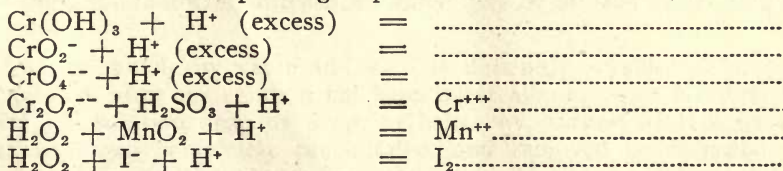


Experiment. Test the action of Na_2O_2 on CrO_2^- . The evolution of oxygen observed in this experiment is due to the decomposition of some of the peroxide.

9. In acid solution H_2O_2 may be reduced by a powerful reducing agent, as H_2S ; but it may also be oxidized by a powerful oxidizing agent, as $\text{Cr}_2\text{O}_7^{--}$.



10. *Problems.* (1) Complete the following equations and state what would be observed in the corresponding experiments:



(2) State how you would prepare $\text{Cr}_2\text{O}_7^{--}$ from Cr^{+++} , $\text{Cr}(\text{OH})_3$ from PbCrO_4 .

(3) Concentrated NH_4OH solution has a slight solvent action on $\text{Al}(\text{OH})_3$ and $\text{Cr}(\text{OH})_3$, but these hydroxides can be reprecipitated by adding an ammonium salt and warming the mixture. Explain.

(4) List in a vertical column all the amphoteric hydroxides you have studied, and write in two more columns the formulas of the corresponding ions which

are formed when the hydroxide is dissolved in excess of a solution of (a) a strong acid, and (b) a strong base.

(5) Examine the position in the Periodic System (Hildebrand, page 257) of each of the elements considered in the preceding problem, and write a brief note on the gradations of properties in each family in which one of these elements occurs. Name additional elements which might be expected to have amphoteric hydroxides.

SECTION V

QUALITATIVE ANALYSIS

ASSIGNMENT 51

THE DEVELOPMENT OF A SCHEME OF ANALYSIS FOR A LIMITED NUMBER OF POSITIVE IONS

(To follow Assignment 38)

1. In Assignment 38 the chemistry of the positive ions already considered was summarized, and the reactions of these ions with various reagents tabulated. We shall now consider how this information may be used in analyzing an unknown solution for these ions.

2. A possible method of analysis would be to devise a separate procedure for each ion, then, if seven ions were to be considered, seven separate portions of the original solution (or substance) would be taken, and each treated by an experiment or series of experiments devised to show whether the particular substance is present or absent in the unknown. Such tests were used in Assignment 31 for Cl^- , SO_4^{--} , and NO_3^- ; in these cases provision was made for neutralizing OH^- , because the presence of OH^- would have interfered with or spoiled the tests. It is to be noted also that the test used for Cl^- is not specific for Cl^- , since any other silver salt which is insoluble in dilute HNO_3 , as silver iodide, would also be precipitated. It is evident that the application of this method (of testing separate portions of the unknown for a particular substance) becomes increasingly difficult as the number of substances which may be present is increased. Also a lengthy procedure is often necessary, especially in testing for certain positive ions when ions of several other metals are present.

3. Accordingly, in systematic qualitative analysis the method has been adopted of using only one portion of the unknown solution in testing for metals, and of preparing from it a pure compound of each metal. Such a process serves to identify the positive constituents and also enables a comparison of the amounts of the various metals to be easily made. The reagents ordinarily used in this process are acids, NH_4OH and NH_4 salts; and therefore separate portions of the unknown are used in testing for H^+ , NH_4^+ , and the various negative ions. (The development of a systematic procedure for the detection of negative constituents will not be considered in this course.)

4. As an illustration we shall discuss the preparation of pure salts of zinc and calcium from an acid solution containing Zn^{++} and Ca^{++} . The Tables in Assignment 38 show the following differences which may be utilized in devising methods of separation:

(1) CaS is soluble in water and ZnS is difficultly soluble. The latter can be precipitated, after the solution has been made alkaline with NH_4OH , by adding $(\text{NH}_4)_2\text{S}$ solution drop by drop, or better by passing in H_2S gas. When the ZnS has been completely precipitated, and removed by filtration, calcium can be tested for in the filtrate and any desired salt of calcium can be prepared. *Experiment.* Test this method by the Procedure given below, with an acid solution which contains both Zn^{++} and Ca^{++} , prepared for example by adding to 100 cc. water in a flask 2 or 3 drops of ZnSO_4 , CaCl_2 and HCl solutions. Repeat, omitting the calcium salt, in order to determine if a satisfactory blank is obtained in the calcium test. *Procedure.* (Be sure that you understand the reason for each detail in the directions.) Add NH_4OH , a few drops at a time, until the mixture after shaking has a distinct odor of NH_3 , pass in H_2S , shake

the mixture thoroughly, and *cautiously* note the odor to determine if H_2S has been added in excess; pass in more H_2S if necessary. (If a large precipitate is obtained, test with litmus and if the solution has become acid add more NH_4OH ; again pass in H_2S until it is present in excess.) Warm the mixture to 50 or 60° , and filter. Test the clear filtrate for calcium by adding $(\text{NH}_4)_2\text{CO}_3$ solution, and heating the mixture almost to boiling. *Note.* If in the analysis of an unknown solution no precipitate is observed in the test for Zn^{++} or Ca^{++} , let the warm solution stand for several minutes before concluding that the ion is absent.

(2) Zn^{++} forms a complex ion with ammonia and Ca^{++} does not. Both carbonates are difficultly soluble in water, but ZnCO_3 , unlike ZnS , dissolves in NH_4OH . Accordingly CaCO_3 can be precipitated by treating the mixture with NH_4OH in excess and $(\text{NH}_4)_2\text{CO}_3$. Write out a Procedure (cf. preceding Paragraph) and note the reason for each of the experimental details.

(3) Zn^{++} is converted into zincate ion by excess of a strong base. Pure NaOH solution would precipitate some of the calcium as $\text{Ca}(\text{OH})_2$ but Na_2CO_3 must also be added to make a satisfactory separation. The laboratory NaOH solution contains some CO_3^{--} but it is better to add Na_2CO_3 .

5. Plan three methods of separating silver and calcium, i. e. of preparing pure salts of silver and of calcium from a mixture of their nitrates. Write out each method, stating why you think it will work; and show your notebook to the instructor.

6. By combining your methods of separation, Paragraphs 4 and 5 devise a "scheme of analysis" for these three positive constituents, silver, zinc and calcium. Test your scheme by *experiments* with very small quantities of solutions of (a) AgNO_3 alone, (b) ZnSO_4 alone, and (c) CaCl_2 alone. In each experiment with a pure salt a satisfactory test should be obtained for one metal and blanks in the tests for the other two.

7. *Experiment.* Predict what will happen when a small quantity of CuSO_4 solution is treated by your scheme of analysis, Paragraph 6, and test your answer by an experiment. Devise a method of including copper in your scheme, and test your method by experiments.

8. Assume that a sodium salt is present in solution with salts of silver, copper, zinc and calcium, and consider how all the sodium originally present, and no more, could be recovered as a pure salt. In other words, include sodium in your scheme. Show your scheme of analysis for the five positive constituents to the instructor. *Question.* With which of the five metals would potassium have been found if it had been present in the original solution?

9. When an unknown solution has been analyzed in this way and a result is inconclusive, owing for example to the small size of the precipitate, a characteristic *confirmatory test* is made whenever possible, such as the dissolving of AgCl in NH_4OH and the reprecipitation with excess HNO_3 , the flame test for calcium, etc.

10. When the *unknowns* are solid salts an important part of the work is the preparation of the solution for analysis. Preliminary experiments with small quantities are performed to determine a method of dissolving the unknown, and conclusions with regard to its nature can often be drawn from the results of these experiments. The salts given out for analysis at this time will dissolve either in water, in dilute acids or in concentrated acids. A discussion of methods of dissolving difficultly soluble salts will be given in Assignment 52.

11. Review your notes in the previous Assignments on the tests for Na^+ , K^+ , NH_4^+ , Cl^- , SO_4^{--} , CO_3^{--} and NO_3^- . Devise a method of testing for

S⁻ based on the formation of H₂S gas, and determine whether your test will apply in the case of a very difficultly soluble sulfide, as CuS.

12. *Analyses* 1, 2 and 3. (*Note.* Do not begin these analyses until the instructor has approved your scheme of analysis for the positive constituents, Paragraphs 6 to 8.) Test for the positive and negative constituents:

H, Ag, Cu, Zn, Ca, Na, K, NH₄
OH, Cl, NO₃, SO₄, CO₃, S.

Record at once each experiment and observation and write down any conclusion that has bearing on the identification. Try to distinguish between large amounts, small amounts, and traces of the different constituents. When you report the result of an analysis to your laboratory instructor show him your notebook record.

13. *Problems.* (1) What negative ions need not be tested for in solutions which contain the following positive ions: (a) H⁺, (b) Ca⁺⁺, (c) Zn⁺⁺, (d) Cu⁺⁺, (e) Ag⁺?

(2) Point out the errors in the following reports:

- (a) A solution known to contain Ag⁺ was reported to contain SO₄⁻ because BaCl₂ gave a white precipitate which did not dissolve in HNO₃.
- (b) A pure sodium salt which dissolved in water to give an alkaline solution was reported to be a sulfate because a white precipitate was obtained on the addition of Ba(NO₃)₂.
- (c) A pure salt which did not dissolve appreciably in water was reported to be zinc nitrate.

ASSIGNMENT 52.

THE STANDARD SCHEME OF ANALYSIS. METHODS OF DISSOLVING DIFFICULTLY SOLUBLE SUBSTANCES

(To follow Assignment 44)

1. In Assignment 51 a number of schemes were considered for the systematic analysis of solutions containing Ag⁺, Cu⁺⁺, Zn⁺⁺, Ca⁺⁺ and Na⁺ (and K⁺). One of the most satisfactory schemes, and the one used in practically all text books, is the following:

To the solution add HCl

Precipitate AgCl	Filtrate (concentration of H ⁺ , 0.3 N): Saturate with H ₂ S gas			
	Precipitate CuS	Filtrate: Boil to expel H ₂ S, * add NH ₄ OH and (NH ₄) ₂ S.		
		Precipitate ZnS	Filtrate: Add (NH ₄) ₂ CO ₃ and warm	
			Precipitate CaCO ₃	Filtrate: Evaporate to dryness, Heat to expel NH ₄ salts. Residue: Na (and K) salts.

* *Note.* It is really not necessary to expel the H₂S; but when additional positive constituents are included in the scheme, and several substances may be precipitated at this point, the observation of the effect of adding NH₄OH in the absence of sulfide often assists in identifying the positive constituents.

2. *Iron and mercury in the scheme of analysis.* From the results of your experiments on the reactions of the ions of iron and mercury, Assignments 43 and 44, predict what would be observed if a solution containing each of the following ions was treated by the scheme of analysis, Paragraph 1: Fe^{++} , Fe^{+++} , Hg^+ , Hg^{++} . *Experiment.* Verify your answers by experiments with dilute solutions of each of these ions. Be sure that the blank tests for the other positive constituents, e. g. Ca^{++} , are negative. *Question.* What mistake has been made if in the experiment with a mercuric salt a black precipitate is obtained with sulfide in the NH_4OH solution?

3. *Separation of ZnS and FeS .* Plan a method of dissolving a mixture of ZnS and FeS and of obtaining pure $\text{Fe}(\text{OH})_3$ and ZnS from the resulting solution (which contains Zn^{++} and Fe^{++}). *Experiment.* Test your method with small amounts of (a) ZnS , (b) FeS , and (c) a mixture of ZnS and FeS . See Assignment 51 Paragraph 4 (1) on the method of precipitating ZnS .

Separation of CuS and HgS . *Experiment.* Prepare a small amount of (a) CuS , and (b) a mixture of CuS and HgS . Treat each of these by the procedure devised in Problem (3), Assignment 44. *Questions.* Why is the sulfur residue black when CuS alone is used, (cf: Assignment 37, Paragraph 10)? Is a confirmatory test for mercuric mercury necessary? For such a test see Assignment 44, Paragraph 3.

Separation of AgCl and HgCl . Devise and confirm by *experiment* a method of determining whether a chloride precipitate is either AgCl or HgCl . If a large amount of HgCl is found and only a small amount of AgCl is present, the method based on the use of NH_4OH solution fails on account of the reduction of Ag^+ by the metallic mercury. Devise a method of detecting silver in the presence of a large amount of HgCl , based on the treatment of the mixture obtained on the addition of NH_4OH , with an oxidizing agent such as bromine solution. *Experiment.* Try your method.

4. The other common positive elements are grouped as follows with the elements already considered.

Division of Metals into Groups for Qualitative Analysis.

Characteristic Metal Name of Group.	Reagents for Precipitation.	Substances Precipitated.
I. Silver Silver Group.	HCl or NH_4Cl and an acid.	AgCl , HgCl , PbCl_2 partially, BiOCl partially.
II. Copper Copper Group.	H_2S in 0.3 N acid.	CuS , PbS , HgS , CdS , Bi_2S_3 , Sulfides of As, Sb, Sn.
III. Zinc Zinc Group.	NH_4OH and $(\text{NH}_4)_2\text{S}$ or NH_4OH in excess and H_2S .	ZnS , $\text{Al}(\text{OH})_3$, $\text{Cr}(\text{OH})_3$, FeS , Fe_2S_3 , MnS , NiS , CoS .
IV. Calcium Calcium Group.	$(\text{NH}_4)_2\text{CO}_3$ and NH_4OH .	CaCO_3 , BaCO_3 , SrCO_3 , a compound of magnesium when alcohol is present.
V. Sodium Sodium Group.	none.	

5. The further separation of the elements has already been illustrated in Paragraphs 2 and 3, but only for two elements in each of three groups. The task

of developing a scheme of analysis becomes increasingly difficult as the number of elements is increased,—mainly on account of the large number of time-consuming experiments which must be made with known mixtures in order to prove that the proposed methods are satisfactory. Therefore if you ever have to make an accurate qualitative analysis of a complicated mixture it will be necessary to consult a standard text-book, such as A. A. Noyes' *Qualitative Chemical Analysis*, and to follow carefully the directions there given. Before attempting to make an analysis with the aid of a book, work through the procedures with known solutions and study the chemistry involved.

6. The present course, however, is not primarily a course in Qualitative Analysis, and a text-book will not be necessary. In the time which remains at our disposal only a limited number of additional elements can be studied in the laboratory. These will be investigated by the same methods as before, and from the tables of reactions it will be possible to develop satisfactory methods for the analysis of simple mixtures.

7. *Analyses Nos. 4, 5 and 6.* In addition to the positive and negative constituents considered in Assignment 51, test for iron, mercurous mercury and mercuric mercury. Do not begin these analyses until the instructor has approved your methods of analysis, Paragraphs 2 and 3. Also study carefully the following paragraphs.

8. *Analysis of an unknown solid.* Record the appearance of the solid. Treat a small portion with water and heat the mixture in a porcelain dish or beaker if the solid does not dissolve readily. Always test the solution with litmus paper. If the solution is neutral, determine if anything has dissolved, either by slowly evaporating a few drops of the clear solution on a watch-glass, or by quickly evaporating a larger quantity of the solution in a porcelain dish.

9. If the solid does not dissolve readily in water, in order to find a satisfactory method of dissolving it, try preliminary experiments, such as are suggested below, with small quantities of the powdered substance. The problem is much simplified if the solid is known to be a single pure substance; for in this case, when a reagent is found to react with some of the solid, the remainder can be made to react in the same way by continued treatment with this reagent.

10. When a method of dissolving the solid has been found, dissolve about 1 gram, and set aside about two-thirds of the solution in order that portions of it may later be used in testing for NH_4^+ and the negative constituents, and in making confirmatory tests. Treat the remainder by the scheme of analysis for the positive constituents; use beakers or flasks in this work, and do not throw away a portion of a solution whenever you have a large volume of it.

11. *Methods of dissolving a difficultly soluble, pure substance.* Observations in these preliminary experiments with small quantities of the solid may be of great assistance in identifying the substance. (In the following, some substances are mentioned which will not be encountered in Analyses 4, 5 and 6).

(1) Treatment with dilute acid. Use $N \text{ HNO}_3$, boil if necessary. Note the odor of any gas evolved. The use of HCl is avoided because AgCl or HgCl might be formed. Similarly BaSO_4 or PbSO_4 might form if H_2SO_4 were used.

(2) Treatment with hot concentrated HCl . If chlorine is evolved a very powerful oxidizing agent is present, such as MnO_2 or PbO_2 . Concentrated HCl dissolves AgCl and HgCl readily, with formation of complex negative ions, but the chlorides precipitate again when water is added to dilute the acid.

(3) Treatment with hot concentrated HNO_3 , a powerful oxidizing agent. The rapid formation of brown gases indicates the presence of a reducing

agent. There is a residue of sulfur after the action of nitric acid on a sulfide, and the solution may contain SO_4^{--} .

(4) Treatment with either (a) a mixture of concentrated HCl and HNO_3 (aqua regia) or (b) bromine water. A few substances, as HgS , are dissolved more readily by these reagents than by concentrated HNO_3 (which is really a more powerful oxidizing agent) on account of the formation of weak electrolytes or complex ions.

Note. Before using for analysis a solution containing concentrated acid evaporate it almost to dryness to remove the excess of acid, and add water.

Question. What happens when H_2S is passed into concentrated HNO_3 or aqua regia?

(5) Treatment with Na_2CO_3 solution to form a carbonate. Use a concentrated solution of Na_2CO_3 in a porcelain dish, cover the dish with a watch-glass and boil for several minutes. Filter and retain the filtrate to test for the negative constituent. Treat the residue with dilute HNO_3 , filter if necessary, and analyze the solution for the positive constituent. Review the action of Na_2CO_3 solution on CaSO_4 , Assignment 32; and, *experiment*, try the above procedure with BaSO_4 .

(6) Special tests. For example, AgCl dissolves in NH_4OH solution, while HgCl turns black; AgCl , when treated with water and H_2S , is transformed into the black Ag_2S , which then may be collected on a filter and dissolved in concentrated HNO_3 .

12. *When the unknown is a mixture of solid salts*, the same method of procedure may be followed in order to determine a method of dissolving the solid completely. However, it is often convenient to analyze separately the portions dissolved in the different operations. For example the mixture might consist of one salt which dissolves readily in water or dilute HNO_3 , and a second salt which does not. If this method is followed, care should be taken to dissolve the first salt completely before continuing the experiments with the residue. *Note.* Frequently when a mixture of two salts, as AgNO_3 and NaCl , is treated with water a reaction takes place.

13. *Problems.* (1) Briefly outline experiments by which you could identify each of the following: AgCl , HgNO_3 , CuO , HgS , ZnCl_2 , $\text{Fe}(\text{OH})_3$, CaCO_3 .

(2 In order to be able to interpret quickly observations made in preliminary experiments on difficultly soluble substances, Paragraph 11, prepare a table, listing in a vertical row all the difficultly soluble compounds, studied thus far, and in a horizontal row the reagents, (a) dilute HNO_3 , (b) hot concentrated HCl , (c) hot concentrated HNO_3 , (d) bromine water (or aqua regia). (e) NH_4OH solution: If the compound is insoluble in a given reagent mark its position in the table with a cross, if soluble write in the formulas of the substances formed when it goes into solution.

ASSIGNMENT 53

LEAD, TIN, ALUMINUM, CHROMIUM, AND BARIUM IN THE SCHEME OF ANALYSIS

(To follow Assignment 47)

Reference. Assignment 52.

1. *Lead in the scheme of analysis.* State what would be observed if a solution of pure $\text{Pb}(\text{NO}_3)_2$ were treated by the scheme of analysis which you used in Assignment 52. Suggest a method of determining whether a white precipitate obtained with HCl contains any PbCl_2 . What would be the result of treating

a mixture of HgS , CuS and PbS with hot 2 N HNO_3 (cf. Assignment 52, Paragraph 3)? Give two reactions which are characteristic of Pb^{++} but not of Cu^{++} , and one reaction which is characteristic of Cu^{++} but not of Pb^{++} . Suggest a method of separating lead from copper and mercury, i. e. of including lead in the scheme of analysis. *Experiment.* Test your method with known solutions.

2. *Tin in the scheme of analysis.* State what would be observed if solutions of (a) stannous tin, (b) stannic tin were treated by the scheme of analysis. In which analytical group would stannous and stannic tin be precipitated? Suggest two methods of separating tin from copper, mercury and lead. *Experiment.* Try one of your methods with known solutions. Repeat the *experiment* in Assignment 46, Paragraph 2 (f), using small amounts of dilute solutions of (a) $\text{Cu}(\text{NO}_3)_2$, (b) SnCl_2 , and (c) a mixture of $\text{Cu}(\text{NO}_3)_2$ and SnCl_2 .

3. *Aluminum and Chromium in the scheme of analysis.* State what would happen if separate solutions of $\text{Al}_2(\text{SO}_4)_3$, $\text{Cr}_2(\text{SO}_4)_3$ and $\text{K}_2\text{Cr}_2\text{O}_7$ were treated by the scheme of analysis. In which analytical group are aluminum and chromium precipitated, and what are the formulas of the substances obtained? How would you prepare from a mixture of ZnS , FeS , $\text{Al}(\text{OH})_3$ and $\text{Cr}(\text{OH})_3$ an alkaline solution containing HZnO_2^- , CrO_2^- and AlO_2^- ? What would be the effect of adding Na_2O_2 to this alkaline solution? Outline a method of showing the presence of aluminum, chromium and zinc in the resulting solution. *Note.* The alkaline solution which contains CrO_4^{--} must not be acidified until the peroxide present has been decomposed by boiling the solution. *Experiment.* Test your method with known solutions containing aluminum and chromium, and chromium alone. *Experiment.* Try the procedure with the reagents, NaOH and Na_2O_2 , and note whether a satisfactory blank test is obtained for aluminum and for zinc.

4. *Barium in the scheme of analysis.* Explain why you might expect barium to be found with calcium in the scheme of analysis. Look up in a table of solubilities, such as is given on the front cover page of Smith's text-book, the solubilities in mols per liter of the hydroxides, carbonates, sulfates and chromates of barium and calcium. Arrange these salts in one column in the order of their solubilities in water. Devise two methods for the separation of calcium and barium.

5. *Procedure for the separation of barium and calcium, after precipitation as carbonates.* *Experiment.* Test the following procedure with a freshly prepared precipitate of (a) BaCO_3 , and (b) CaCO_3 . To dissolve the carbonate precipitate pour repeatedly through the filter a 10 cc. portion of hot 3 N acetic acid, and use a little more acetic acid if the precipitate does not dissolve completely. Add 20 cc. $\text{N NH}_4\text{Ac}$, and heat the solution to boiling in a flask. Measure out 15 cc. $\text{N Na}_2\text{CrO}_4$ and add it, a little at a time, heating and shaking the mixture after each addition. Finally heat the mixture at $90^\circ - 100^\circ$ for one or two minutes, and shake it at the same time. Filter, even if you cannot see a precipitate, remove the filtrate and wash the precipitate with cold water. (Pale yellow precipitate, presence of *barium*.) To confirm the presence of barium, dissolve the precipitate by pouring hot HCl through the filter, evaporating to a small volume, and applying the flame test. To test for *calcium* in the filtrate, make the solution alkaline with NH_4OH , add $(\text{NH}_4)_2\text{CO}_3$, or ammonium oxalate, and heat the mixture just to boiling. *Note.* The separation depends on the fact that BaCrO_4 is much less soluble in water than is CaCrO_4 . If the BaCrO_4 is not precipitated slowly in a hot acid solution, as directed, the precipitate will be so finely divided that it will run through the filter.

6. *Analyses Nos. 7, 8, 9, etc.* Test for all the positive and negative constituents you have studied. Verify your results by experiments with known substances.

7. Problems. (1) Complete the table of the behavior of difficultly soluble substances towards various reagents, Assignment 52 Problem (2), by the addition of the difficultly soluble substances studied in Assignments 45-47 and 53.

(2) Point out the errors in the following reports:

- (a) Mercury is reported to be present because a black residue remained when the sulfides of the copper group were boiled with 2 N HNO_3 .
- (b) Lead is reported to have been found in the silver group but not in the copper group.
- (c) In the analysis referred to in (b) a black precipitate was observed in testing for the zinc group, although no test for iron was obtained. What errors in the method of analysis would produce this result?
- (d) Aluminum is reported to be present in the zinc group, but the notebook shows the following records: on precipitating the zinc group a greenish precipitate was obtained on the addition of NH_4OH , later a yellow solution resulted when Na_2O_2 was added; when this solution was acidified there was evolution of gas and the yellow color disappeared; on the addition of NH_4OH a precipitate was formed.

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